Protection and polymerization of functional monomers: 8. Anionic living polymerization of 4-[2-(trialkyl)silyloxyethyl]styrene as protected 4-(2-hydroxyethyl)styrene*

Akira Hirao, Akihiko Yamamoto, Katsuhiko Takenaka, Kazuo Yamaguchi and Seiichi Nakahama
Department of Polymer Chemistry, Faculty of Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152, Japan
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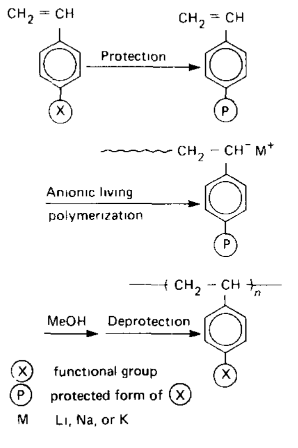
Anionic polymerizations of 2-(4-vinylphenyl)ethoxy(trialkyl)silanes and 2-(4-vinylphenyl)ethoxy(t-butoxydimethyl)silane were investigated with oligo(α-methylstyryl)dilithium or -dipotassium as initiator in tetrahydrofuran at −78°C. These monomers readily polymerized to form 'living polymers'. Subsequent deprotection of the silyl groups from the resulting polymers gave poly[2-(4-vinylphenyl)ethanol]s of the desired molecular weights with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.05$–$1.21$). The living polymers of the silyl ethers of 2-(4-vinylphenyl)ethanol can initiate further polymerization of either styrene or α-methylstyrene, yielding new block copolymers containing 2-(vinylphenyl)ethanol blocks.

(Keywords: poly[2-(4-vinylphenyl)ethanol]; living polymer; anionic polymerization; 2-(4-vinylphenyl)ethoxy(trialkyl)silane; block copolymer)

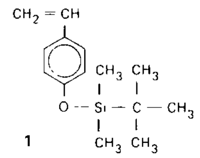
INTRODUCTION

For a few years we have been investigating the synthesis of linear functional polymers having a high uniformity of chain length as well as a predictable molecular weight[1-7]. Our approach involves the anionic living polymerization of monomers with suitably protected functional groups, followed by the removal of the protecting groups, as illustrated in the following scheme where a styrene derivative is given as an example.



It is of course essential that the functional group can be satisfactorily protected during the course of the anionic polymerization, and that the protective group can be readily and completely removed after the polymerization, to regenerate the original functional group.

We have found that some trialkylsilyl groups satisfy the above-mentioned criteria for the protection of hydroxyl and amino functions attached to styrene derivatives. The new silyl-protected monomers such as **1** and **2** undergo anionic living polymerization. By subsequent removal of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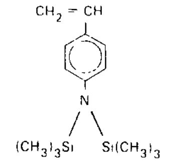
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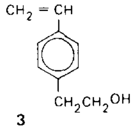
the silyl groups, poly(4-vinylphenol) and poly(4-vinylaniline) of known molecular weights and narrow molecular weight distributions have been obtained[1-4]. These polymers are so far difficult to prepare by any other method.

In the previous communication[3], we reported that the trimethylsilyl ether (**4a**) of 2-(4-vinylphenyl)ethanol (**3**) was anionically polymerized in a living fashion free from chain transfer and termination. The resulting polymer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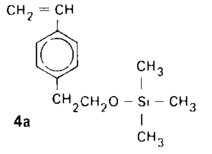
4a

had a predictable molecular weight and a narrow molecular weight distribution. Very recently, however, it occurred to us that the trimethylsilyl protective groups might undergo undesirable side reactions which cause gradual destruction of the living ends of poly(**4a**) with time.

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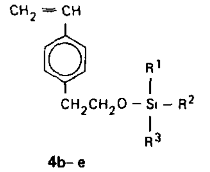
Therefore, we rechecked in this work the living character of the polymerization of **4a**. In addition, the possibility of anionic living polymerizations of the following silyl ethers of **3** will be described for comparison.



4b–e

4b $R^1 = R^2 = R^3 = C_2H_5$
4c $R^1 = R^2 = CH_3$, $R^3 = CH(CH_3)_2$
4d $R^1 = R^2 = CH_3$, $R^3 = C(CH_3)_3$
4e $R^1 = R^2 = CH_3$, $R^3 = OC(CH_3)_3$

EXPERIMENTAL

Materials

4-Chlorostyrene was kindly supplied by Hokko Chemical Industry Co. Ltd. It was distilled at 52–54°C (5 mbar) over calcium hydride. Commercial α-methylstyrene, styrene, pyridine, and t-butyl alcohol were purified by distillation over calcium hydride. Tetrahydrofuran (THF) was used as a solvent in all polymerization experiments and was distilled from sodium wire and then from sodium naphthalide solution. Naphthalene was purified by sublimation. Butyllithium was obtained from Nakarai Chemical Co. Ltd. Hexamethyldisilazane, dimethyldichlorosilane, triethylsilyl chloride and t-butyldimethylsilyl chloride were obtained from Shinetsu Chemical Co. Ltd and were used without further purification. Lithium and potassium naphthalides were prepared from lithium and potassium, respectively, and naphthalene in THF at 20°C for 10 h. The reaction mixture was filtered and the green-coloured filtrate was titrated to a colourless endpoint by using standardized 1-octanol in THF. Oligo(α-methylstyryl-) dilithium and -dipotassium were prepared, just prior to polymerization, from lithium and potassium naphthalides, respectively, and 2–4 moles of α-methylstyrene at 30°C for 1 min and then at -78°C for 5–10 min. The preparations of lithium and potassium naphthalides and oligo(α-methylstyryl)dilithium and -dipotassium were carried out under high vacuum ($\approx 10^{-6}$ mbar) in reactors equipped with breakseals.

i-Propyldimethylsilyl chloride

A mixture of i-propyl chloride (13.4 g, 130 mmol), dimethyldichlorosilane (40.7 g, 330 mmol) and magnesium (4.2 g, 170 mmol) in THF (200 ml) was refluxed for 15 h under a nitrogen atmosphere. The mixture was filtered and the precipitate was washed with dry THF under a nitrogen atmosphere. The THF extracts were combined with the filtrate, and the mixture was fractionally distilled at 105–110°C to give 7.1 g (39%) of i-propyldimethylsilyl chloride as a colourless liquid. ^{1}H n.m.r. ($CDCl_3$): $\delta = 1.00$ (s, 6H, Si–CH_3), 1.20–1.90 (m, 1H, Si–CH–), 1.67 (s, 6H, Si–$C(CH_3)_2$).

t-Butoxydimethylsilyl chloride

To a stirred solution of dimethyldichlorosilane (22.7 g, 176 mmol) in pentane (150 ml) was slowly added t-butyl alcohol (13.0 g, 176 mmol) and triethylamine (16.7 g, 165 mmol) in pentane (150 ml) over a 1 h period at 0°C under an atmosphere of nitrogen. After the mixture was stirred for 5 h at room temperature, it was filtered and the white solid was washed with pentane. The pentane extracts were combined with the filtrate and the mixture was fractionally distilled at 60–64°C (120 mbar) to give 18.3 g (69%) of t-butoxydimethylsilyl chloride as a colourless liquid. ^{1}H n.m.r. (CCl_4): $\delta = 0.41$ (s, 6H, Si–CH_3); 1.33 (s, 9H, C–CH_3).

2-(4-Vinylphenyl)ethanol (**3**) *and 2-(4-vinylphenyl)-ethoxy(trimethyl)silane* (**4a**)

Monomers **3** and **4a** were prepared as reported elsewhere[3,8].

2-(4-Vinylphenyl)ethoxy(triethyl)silane (**4b**)

To a mixture of **3** (5.5 g, 37 mmol) and imidazole (5.4 g, 80 mmol) in *N*,*N*-dimethylformamide (DMF) (20 ml), triethylsilyl chloride (5.6 g, 37 mmol) in DMF (10 ml) was added dropwise at 0°C. The reaction mixture was stirred at 0°C for 1 h and then at 20°C overnight. After addition of ether, the mixture was washed with 5% NaOH solution and then with water, and dried over anhydrous $MgSO_4$. After evaporation of the ether, the crude product was purified by fractional distillation. Yield: 69%; b.p. 100–105°C (1 mbar). ^{1}H n.m.r. (CCl_4) $\delta = 0.15$–0.97 (m, 15H, Si–CH_2CH_3), 2.63 (t, 2H, $J = 7$ Hz, C_6H_4–CH_2–), 3.63 (t, 2H, $J = 7$ Hz, Si–O–CH_2–), 5.01, 5.49 (2d, 2H, $J = 11, 18$ Hz, $CH_2=$), 6.56 (2d, 1H, CH=), 6.94, 7.16 (2d, 4H, $J = 8$ Hz, C_6H_4, a, b).

2-(4-Vinylphenyl)ethoxy(i-propyldimethyl)silane (**4c**)

A reaction similar to the above was run with **3**, imidazole and i-propyldimethylsilyl chloride (5.1 g, 37 mmol) in DMF. After the reaction was completed, the product was distilled at 89–91°C (3 mbar). Yield: 67%. ^{1}H n.m.r. (CCl_4): $\delta = 0.20$ (s, 6H, Si–CH_3), 1.31 (s, 6H, Si–$CH(CH_3)_2$), 1.00–1.50 (m, Si–CH), 3.11 (t, 2H, $J = 7$ Hz, C_6H_4–CH_2–), 4.14 (t, 2H, $J = 7$ Hz, Si–O–CH_2–), 5.55, 6.04 (2d, 2H, $J = 11, 18$ Hz, $CH_2=$), 7.10, (2d, 1H, CH=), 7.48, 7.70 (2d, 4H, $J = 8$ Hz, C_6H_4, a,b).

2-(4-Vinylphenyl)ethoxy(t-butyldimethyl)silane (**4d**)

A reaction similar to the above was run with **3**, imidazole and t-butyldimethylsilyl chloride (5.6 g, 37 mmol) in DMF. After the reaction was completed, the product was distilled at 93–95°C (2 mbar). Yield: 75%. ^{1}H n.m.r. (CCl_4): $\delta = 0.20$ (s, 6H, Si–CH_3), 1.12 (s, 9H, Si–C–CH_3), 3.02 (t, 2H, $J = 7$ Hz, –C_6H_4–CH_2–), 4.05 (t, 2H, $J = 7$ Hz, Si–O–CH_2–), 5.42, 5.92 (2d, 2H, $J = 10$, 18 Hz, $CH_2=$), 6.96 (2d, 1H, CH=), 7.35, 7.55 (2d, 4H, $J = 8$ Hz, C_6H_4, a, b).

2-(4-Vinylphenyl)ethoxy(t-butoxydimethyl)silane (**4e**)

A reaction similar to the above was run with **3**, imidazole and t-butoxydimethylsilyl chloride (6.2 g, 37 mmol) in DMF. After the reaction was completed, the product was distilled at 83–85°C (2 mbar). Yield: 53%. ^{1}H n.m.r. (CCl_4); $\delta = 0.20$ (s, 6H, Si–CH_3), 1.43 (s, 9H, Si–O–C–CH_3), 3.08 (t, 2H, $J = 7$ Hz, C_6H_4–CH_2–), 4.01 (t, 2H, $J = 7$ Hz, Si–O–CH_2–), 5.36, 5.81 (2d, 2H, $J = 10$, 18 Hz, $CH_2=$), 6.91, (2d, 1H, CH =), 7.31, 7.53 (2d, 4H, $J = 8$ Hz, C_6H_4, a, b).

Purification

In order to remove impurities in monomer **4a**, benzylmagnesium chloride (5.0 ml, 0.5 M solution in THF) was added to **4a** (5.0 g, 23 mmol) at 0°C under a nitrogen atmosphere. The mixture was stirred for 10 min and degassed. THF and **4a** were then distilled on a vacuum line into ampoules fitted with breakseals. Purified **4a** in THF thus obtained was stored at −30°C until used. The other monomers (**4b–e**, styrene and α-methylstyrene) were purified in a similar manner.

Polymerizations

All operations were carried out under high vacuum (10^{-6} mbar) in an all-glass apparatus equipped with breakseals. All the polymerizations were carried out at −78°C with shaking. The polymers from **4b–e** were precipitated in water and filtered, redissolved in THF, and precipitated into methanol–water (5/1, v/v) twice more. Then they were freeze-dried. The polymers from **4a** were precipitated, after quenching with methanol–2 N HCl (1/1, v/v), by addition to an excess of water. They were filtered, redissolved in methanol, precipitated into water twice more and were dissolved in 1,4-dioxane and dried by freeze-drying.

Block copolymerizations and the resulting block copolymer treatments were also performed in a similar manner.

Determination of actual contents of **5a–e** *in the polymerization systems*

The operations were conducted under vacuum by a method similar to that described by Morton, Rembaum and Hall[9].

Deprotection of silyl protecting groups from the poly(**4b–e**)

Poly(**4b**), -(**4c**) or -(**4e**) (1.0 g) was dissolved in 1,4-dioxane (20 ml) containing a few drops of concentrated HCl. The mixture was heated to 80°C for 1 h and poured into an excess of water. The polymer was recovered by filtration, washed with water, redissolved in 1,4-dioxane, precipitated into hexane, and then dried. In the case of poly(**4d**), more acidic conditions were needed for deprotection. Thus, the polymer was dissolved in 2 N HCl aqueous 1,4-dioxane. The mixture was heated to 50°C for 3 h, and subsequently treated as above to give poly[2-(4-vinylphenyl)ethanol] in an almost quantitative yield.

The ^{1}H n.m.r. and i.r. spectra of the resulting polymers showed signals and absorptions consistent with poly[2-(4-vinylphenyl)ethanol]. Neither signal nor band corresponding to the silyl protecting groups could be detected at all.

Acetylation of poly[2-(4-vinylphenyl)ethanol]

To 0.5 g polymer in 6 ml dry pyridine under a nitrogen atmosphere, 3 ml acetic anhydride was added over 5 min at 0°C. The reaction mixture was stirred at 0°C for 24 h and then at 20°C for an additional 24 h, and poured into water. The polymer precipitated was recovered by filtration, dissolved in THF, reprecipitated twice into methanol–water (1/1, v/v), and freeze-dried. The ^{1}H n.m.r. specrrum indicated a complete acetylation of poly[2-(4-vinylphenyl)ethanol].

Measurements

^{1}H n.m.r. spectra were recorded using a Jeol JNM-PMX 60 spectrometer. I.r. spectra were recorded on a Jasco IR-G spectrometer. Gel permeation chromatograms (g.p.c.) were obtained on a Toyosoda HLC-802 instrument with u.v. or refractive index detection, THF being the eluent. Molecular weights were measured on a Corona 117 vapour pressure osmometer (v.p.o.) in benzene.

RESULTS AND DISCUSSION

A large number of protective methods for the hydroxyl group have so far been known[10]. Among them, those using the trialkylsilyl protective groups are of particular interest to us because the resulting silyl ethers as protected forms are stable towards the highly reactive bases, some of which are often used a anionic initiators. This suggests that the hydroxyl group can be satisfactorily protected with the trialkylsilyl groups during the course of anionic polymerization.

Anionic polymerization of **4a**

The anionic polymerization of **4a** was carried out in THF at −78°C with lithium naphthalide, oligo(α-methylstyryl)lithium or -dipotassium as an initiator. The results are summarized in *Table 1*. Since the partial cleavage of trimethylsilyl ether in the resulting polymer was always observed after two reprecipitations using the THF–methanol system, we converted the resulting polymer to poly[2-(4-vinylphenyl)ethyl acetate] by removal of the trimethylsilyl groups followed by esterification with acetic anhydride. The ^{1}H n.m.r. spectra confirm that the two steps proceed quantitatively. The acetylated polymer thus obtained was then characterized.

As can be seen in *Table 1*, there is good agreement between the values of $\bar{M}_n$ for the acetylated polymers measured by v.p.o. and the calculated values based on the assumption that living polymers are obtained by difunctional initiators. The g.p.c. curves indicate that the polymers all possess narrow molecular weight distributions with the values of $\bar{M}_w/\bar{M}_n$, calculated by

Table 1 Anionic polymerization of **4a** in THF at −78°C for 5–30 min[a]

4a (mmol)	Initiator (mmol)		α-Methylstyrene (mmol)	$\bar{M}_n$ calc.[b]	$\bar{M}_n$ obs.[c]	$\bar{M}_w/\bar{M}_n$[d]
5.35	Butyllithium	0.132	0.747	9000	12000	1.12
5.20	Lithium naphthalide	0.125	–	16000	18000	1.20
4.89	Potassium naphthalide	0.0886	0.335	23000	20000	1.12
9.13	Lithium naphthalide	0.133	–	28000	25000	1.13
8.99	Lithium naphthalide	0.120	–	31000	25000	1.21
10.25	Lithium naphthalide	0.0680	–	62000	69000	1.16

[a] Yields of polymers were 95–100%

[b] Calculated for poly[2-(4-vinylphenyl)ethyl acetate]

[c] Vapour pressure osmometry in benzene

[d] Calculated from g.p.c. curves according to Tung's method[11]

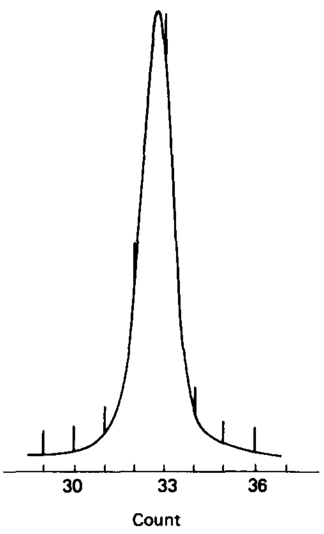


Figure 1 Molecular weight distribution for poly[2-(4-vinylphenyl)ethyl acetate], $\bar{M}_n$ obs. (v.p.o.) = 12 000, $\bar{M}_w/\bar{M}_n = 1.12$ (see *Table 1*)

Table 2 Results of titration for initiator and **5a–e** in THF at −78°C[a]

Time (h)	Initiator[b] (mmol)	5 (mmol)	Carbanion survived[c] (%)
0.5	0.112	**5a** 0.0850	76
0.5	0.104	**5b** 0.0980	94
24	0.0918	**5b** 0.0905	99
0.5	0.145	**5c** 0.154	~100
24	0.118	**5c** 0.117	99
0.5	0.0731	**5d** 0.0726	99
24	0.104	**5d** 0.103	99
0.5	0.0770	**5e** 0.0781	~100
24	0.126	**5e** 0.122	97

[a] Conversion of polymer: 100%
[b] Oligo(α-methylstyryl)dipotassium
[c] Calculated from the ratio of [5] to [initiator]

Tung's method[11] using a polystyrene calibration, in the range of 1.12 to 1.21. A representative g.p.c. profile is illustrated in *Figure 1*. These results indicate the rapidity of initiation and the absence of chain transfer and termination in the polymerization.

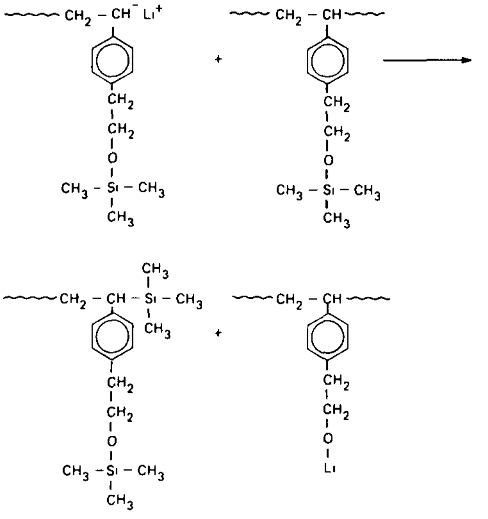
However, at the end of the polymerization we observed that a characteristic colour (brownish orange with Li^+ and dark red with K^+) of the polymerization mixture gradually faded with time, indicating the destruction of the growing chain end. The concentration of the living ends was therefore determined by direct *in situ* titration of the coloured solution. By the titration, 30–50% losses of the living ends were detected after 30–60 min polymerizations, although the values depended on the ratio of monomer to initiator, counterion and polymerization time. Accordingly, some side reactions annihilated the living ends.

If such reactions could occur during the polymerization, they would result in losses of initiator and active growing ends, so that the actual molecular weight would be higher than predicted and the molecular weight distribution would be broader than actually observed. The results shown in *Table 1* clearly exclude such possibilities, and there is little, if any, influence of the side reactions on the polymerization. Since the polymerization appears almost instantaneous and, as the titration indicated, the side reactions are slow and far from complete even after 30 min, they may occur mainly after then end of the polymerization.

Since it is known that alkyllithium compounds cleave trialkylsily ethers[12]

$$R^1Li + R^2O-\overset{|}{\underset{|}{Si}}- \longrightarrow R^1-\overset{|}{\underset{|}{Si}}- + R^2OLi \quad (1)$$

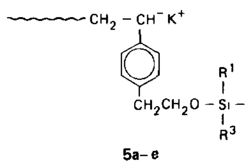
the side reaction would most likely be one between the active growing end and a trimethylsilyl ether group in the polymer:



Anionic polymerization of **4b–e**

New silyl-protected monomers **4b–e** were readily prepared by treating **3** with the corresponding silyl chlorides and 2 moles of imidazole in DMF. Yields were usually either excellent or nearly quantitative (by g.c. indication; 70–90% after isolation). The monomers are stable and resistant to hydrolysis under either neutral or basic conditions.

The anionic polymerizations of these monomers were carried out at −78°C in THF mainly with oligo(α-methylstyryl)dipotassium as an initiator. Throughout the polymerizations, a dark red colour, characteristic of the polystyryl anions (**5b–e**), was observed and remained unchanged as long as 24 h at the same temperature.



5a–e

5a $R^1 = R^2 = R^3 = CH_3$
5b $R^1 = R^2 = R^3 = C_2H_5$
5c $R^1 = R^2 = CH_3$, $R^3 = CH(CH_3)_2$
5d $R^1 = R^2 = CH_3$, $R^3 = C(CH_3)_3$
5e $R^1 = R^2 = CH_3$, $R^3 = OC(CH_3)_3$

The concentrations of **5a–e** could be determined by colorimetric *in situ* titration of the coloured reaction solutions. Typical results are shown in *Table 2*, which compares the concentrations of **5a–e** (at −78°C after 0.5 and 24 h) with those of the initiators. As can be seen, losses of **5b–e** are absent within analytical error, indicating that **5b–e** are stable under our conditions. This is in contrast to the fact that the active end of **5a** is gradually destroyed with time.

The polymers of **4b–e** were recovered by precipitation into excess methanol. Yields were almost quantitative. After two additional reprecipitations, the silyl protecting groups stayed intact, as indicated by the ^1H n.m.r. spectra of the resulting polymers. They were therefore

Table 3 Anionic polymerizations of **4b–e** in THF at −78°C for 5–30 min[a]

Monomer (mmol)	Initiator (mmol)	α-Methylstyrene (mmol)	$\bar{M}_n$ calc.	$\bar{M}_n$ obs.[b]	$\bar{M}_w/\bar{M}_n$[c]
4b 7.60	BuLi[d] 0.183	0.337	11 000	12 000	1.06
4b 4.13	K-Nap[e] 0.166	0.355	14 000	12 000	1.17
4b 3.55	K-Nap 0.124	0.413	16 000	13 000	1.13
4b 3.05	K-Nap 0.0569	0.151	29 000	29 000	1.20
4c 3.90	K-Nap 0.152	0.298	13 000	14 000	1.14
4c 3.73	K-Nap 0.120	0.557	17 000	21 000	1.08
4c 9.18	K-Nap 0.0842	0.239	55 000	54 000	1.11
4d 4.83	BuLi 0.0754	0.460	18 000	19 000	1.06
4d 5.00	BuLi 0.0684	0.443	20 000	22 000	1.05
4d 3.41	K-Nap 0.0728	0.326	26 000	23 000	1.10
4d 6.46	K-Nap 0.0622	0.318	56 000	45 000	1.13
4e 3.37	K-Nap 0.108	0.180	18 000	13 000	1.09
4e 3.77	K-Nap 0.0846	0.150	25 000	26 000	1.19
4e 4.23	K-Nap 0.0618	0.340	39 000	32 000	1.10

[a] Yields of polymers were 90–100%
[b] Vapour pressure osmometry in benzene
[c] Calculated from g.p.c. curves according to Tung's method[11]
[d] Butyllithium
[e] Potassium naphthalide

characterized as recovered without further treatment. The results are summarized in *Table 3*.

It can be seen that the measured and predicted molecular weights are in good agreement in all cases studied here. The molecular weight distributions of these polymer samples (*Figure 2*) were very narrow; the $\bar{M}_w/\bar{M}_n$ values were in the range between 1.05 and 1.20. These results indicate that the polymerizations of **4b–e** proceed in the absence of transfer and termination. The narrow molecular weight distribution provided convincing evidence that initiation is much faster than propagation. Accordingly, together with the results of titration indicating that **5b–e** are stable, these systems are classified as truly living. Further evidence for their living character is provided by successful preparation of block copolymers which will be discussed later.

Thus, triethyl-, i-propyldimethyl-, t-butyldimethyl- and t-butoxydimethylsilyl groups satisfactorily protect the hydroxyl proton of **3** under anionic polymerization conditions. The silyl ethers of **3** carrying these groups (and their polymers) are stable towards both anionic initiators and growing carbanions. In contrast, the trimethylsilyl ether (**4a**) is unsatisfactory as a protected monomer, since it is gradually cleaved by these nucleophiles (equation (2)). The success of the above silyl groups, except for the trimethylsilyl one, as protecting functions is at least in part due to the steric bulkiness of the substituents around the silicon atom.

Deprotection of silyl protecting groups from polymers

Among the silyloxyl pendants in poly(**4a**)–poly(**4e**), the trimethylsilyloxyl group is the most labile towards hydrolysis. It was instantly and completely cleaved by treatment at room temperature with aqueous 1,4-dioxane containing a small amount of acetic acid. The triethyl-, i-propyldimethyl- and t-butoxydimethylsilyl counterparts were more stable to hydrolysis, but were still readily cleaved by treatment with aqueous 1,4-dioxane containing a few drops of concentrated HCl at 80°C for 1 h. More acidic conditions (2 N HCl aqueous 1,4-dioxane, 50°C, 3 h) were needed to cleave the t-butyldimethylsilyloxyl group, which was, as expected, the most stable.

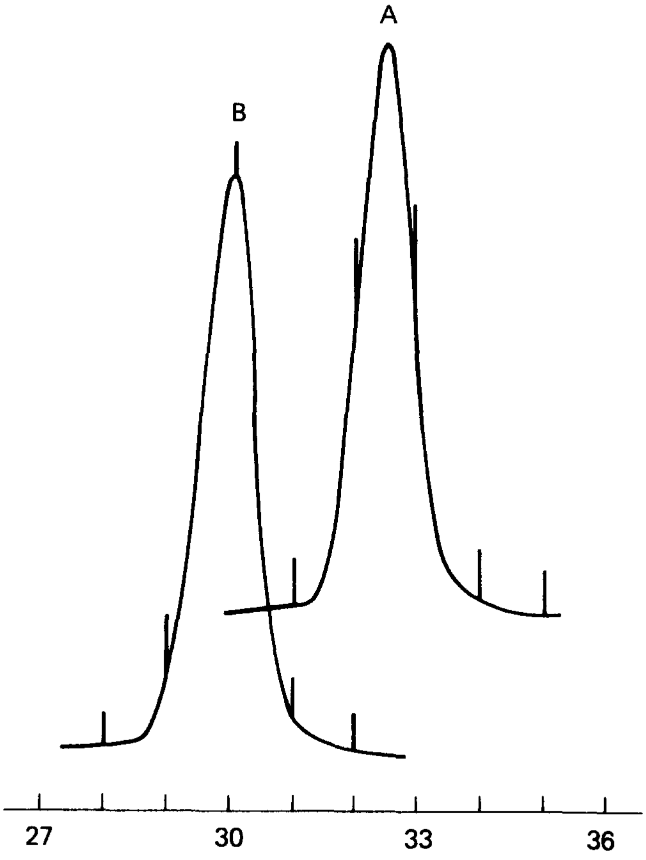


Figure 2 Molecular weight distributions for (A) poly[2-(4-vinylphenyl)ethoxy(triethyl)silane], $\bar{M}_n$ obs. (v.p.o.) = 12 000, $\bar{M}_w/\bar{M}_n$ = 1.06, and (B) poly[2-(4-vinylphenyl)ethoxy(t-butoxydimethyl)silane], $\bar{M}_n$ obs. (v.p.o.) = 32 000, $\bar{M}_w/\bar{M}_n$ = 1.10 (see *Table 3*)

Free poly(**3**) was isolated in an almost 100% yield by precipitation in water after the above treatment. In all cases quantitative removal of the silyl groups was confirmed by i.r. and ^{1}H n.m.r. spectra of the resulting polymers. *Figure 3* shows the representative ^{1}H n.m.r. spectra before and after the hydrolysis of poly(**4d**). The spectrum B shows the expected structure of poly(**3**) and no signals corresponding to the silyl protecting group are detected.

In order to check the molecular weight and its distribution of the poly(**3**) samples thus obtained, some of them were converted into poly[2-(4-vinylphenyl)ethyl acetate] so as to solubilize them in THF and benzene for g.p.c. and v.p.o. measurements. The g.p.c. traces of the acetylated polymers all showed a single narrow peak ($\bar{M}_w/\bar{M}_n \sim 1.1$) eluting in a reasonable molecular weight region. This confirms the absence of main chain degradation during the deprotection step under acidic conditions. More reliable data were obtained by v.p.o.; little difference in the degree of polymerization was found between the original protected polymers and their deprotected and then acetylated forms as shown in *Table 4*. Accordingly, the poly(**3**) obtained by the anionic living polymerization of silyl-protected monomers (**4b–e**), followed by the removal of the protecting groups, should be a linear polymer of well defined structure, known molecular weight and narrow molecular weight distribution.

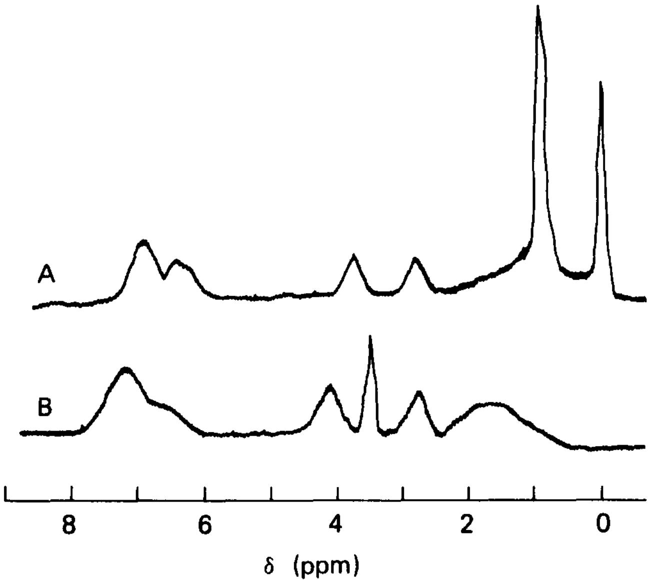


Figure 3 ^{1}H n.m.r. spectra of (A) poly[2-(4-vinylphenyl)ethoxy(t-butyldimethyl)silane] (in CCl_4), and (B) poly[2-(4-vinylphenyl)ethanol (in CD_3OD) obtained after hydrolysis of poly[2-(4-vinylphenyl)ethoxy-(t-butyldimethyl)silane]

Table 4 Degrees of polymerization of poly(**4**) and its acetylated form

	Poly(**4**)		Acetylated polymer[a]	
	DP[b]	$\bar{M}_w/\bar{M}_n$	*DP*[b]	$\bar{M}_w/\bar{M}_n$
Poly(**4b**)	46	1.10	43	1.12
Poly(**4c**)	129	1.26	127	1.24
Poly(**4d**)	76	1.10	78	1.15

[a] Obtained by deprotection of poly(**4**) followed by acetylation (see text)
[b] Determined by vapour pressure osmometry in benzene

Block copolymerization

The synthesis of precisely tailored block copolymers has stimulated a great deal of interest from both chemical and industrial points of view. Such polymer synthesis is possible only through sequential living polymerization of different monomers. Indeed, several interesting block copolymers have successfully been prepared by this method[13].

In the preceding section, we have demonstrated the living character of the anionic polymerizations of protected monomers, **4b–e**. The application of these polymerizations to the synthesis of block copolymers is interesting, since it can produce novel block copolymers with hydroxyl functionalities in which each block has a predictable molecular weight and a narrow molecular weight distribution.

B–A–B type triblock copolymers were prepared by the sequential polymerization of monomer A (**4b**, **4c**, **4d** or **4e**) and monomer B (styrene or α-methylstyrene). The polymers were obtained in virtually quantitative yields. The results are summarized in *Table 5*.

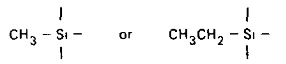
G.p.c. analysis (*Figure 4*) showed that the peaks of the polymers obtained at the first stage shifted completely towards higher molecular weight after the addition of the second monomer and that the resulting polymers possessed a single and narrow molecular weight distribution without any observable peak corresponding to the first block. The observed $\bar{M}_n$ values of the block copolymers were in reasonable agreement with those expected from the monomer-to-initiator ratios. The ^{1}H n.m.r. spectra showed the presence of each block in the resulting polymers. The observed intensity ratios of the

Table 5 Block copolymerizations of **4** with styrene or α-methylstyrene at −78°C in THF with oligo(α-methylstyryl)dipotassium

			Block copolymer[a]			
			Calculated values		Observed values[b]	
Type	A monomer	B monomer	$\bar{M}_n$	[A]/[B]	$\bar{M}_n$	[A]/[B]
B–A–B	**4b**	Styrene	42 000	15/85	40 000	14/86
B–A–B	**4c**	Styrene	47 000	19/81	53 000	21/79
B–A–B[c]	**4d**	α-Methylstyrene	52 000	18/82	45 000	18/82
B–A–B	**4e**	Styrene	44 000	19/81	40 000	17/83
A–B–A	**4b**	Styrene	24 000	25/75	22 000	23/77
A–B–A	**4c**	Styrene	29 000	31/69	32 000	30/70
A–B–A	**4d**	Styrene	30 000	31/69	27 000	31/69
A–B–A	**4e**	Styrene	30 000	26/74	28 000	22/78
A–B[d]	**4d**	α-Methylstyrene	59 000	15/85	66 000	14/86
A–B[d]	**4d**	α-Methylstyrene	88 000	12/88	89 000	11/89
B–A[d]	**4d**	α-Methylstyrene	33 000	47/53	39 000	55/45

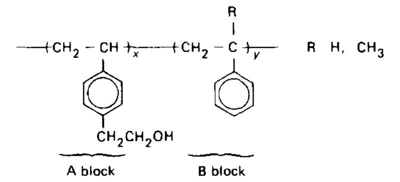
[a] Yields: 90–100%; $\bar{M}_w/\bar{M}_n$: 1.05–1.20; not deprotected
[b] Determined by v.p.o. and ^{1}H n.m.r.
[c] Initiated by oligo(α-methylstyryl)dilithium prepared from lithium naphthalide and α-methylstyrene
[d] Initiated by oligo(α-methylstyryl)lithium prepared from butyllithium and α-methylstyrene

aromatic to



$$CH_3-\overset{|}{\underset{|}{Si}}- \quad \text{or} \quad CH_3CH_2-\overset{|}{\underset{|}{Si}}-$$

protons were found to be almost equal to those calculated from both monomers fed into the polymerizations. These analyses clearly indicate the formation of the expected block copolymers free of homopolymers. It follows that the tailored block copolymers with hydroxyl functionalities can be made by our method (see the formula below). The successful preparation of the block copolymers also provides strong evidence for the living character of the anionic polymerizations of **4b–e**.



With **4a**, on the other hand, the less stable living end of poly(**4a**) presents the following problem for the preparation of block copolymers. Some portions of the bifunctional living ends of poly(**4a**) would be terminated at one or both ends before the addition of second monomer, so that the final triblock copolymer would be contaminated by a free homopolymer of **4a** and a diblock copolymer. Curve B in *Figure 5* shows the g.p.c. curve of an example obtained by the sequential polymerization of **4a** and α-methylstyrene. Curve B for the final product consists of three peaks, indicating that it is a mixture of the starting homopolymer of **4a**, A–B block copolymers and the desired B–A–B component. Therefore it was difficult to prepare a pure block copolymer of B–A–B structure by the method using the polymeric anion of **4a**.

In contrast, the block copolymer of A–B–A type could be successfully obtained by the opposite sequence of monomer addition (first α-methylstyrene and then **4a**) to a THF solution of lithium naphthalide at −78°C. G.p.c., v.p.o. and ^{1}H n.m.r. analyses of the resulting polymers supported the formation of the expected block copolymers, as shown in *Table 6* and *Figure 6*. Thus, the synthesis of block copolymers by the use of **4a** imposes

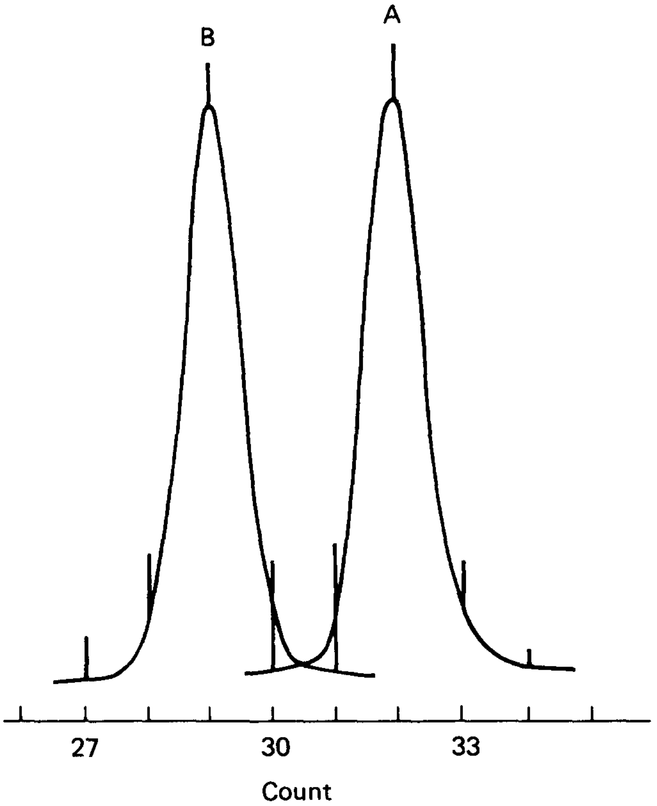


Figure 4 Molecular weight distributions for (A) poly[2-(4-vinylphenyl)ethoxy(t-butyldimethyl)silane] initially polymerized, $\bar{M}_n$ obs. (v.p.o.) = 15 000, and (B) poly[α-methylstyrene-*b*-2-(4-vinylphenyl) ethoxy(t-butyldimethyl)silane-*b*-α-methylstyrene], $\bar{M}_n$ obs. (v.p.o.) = 45 000 (see *Table 5*)

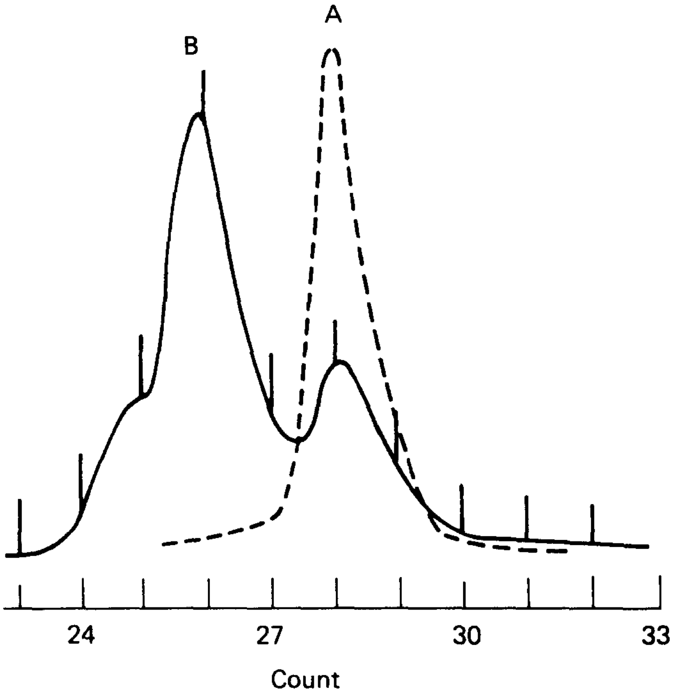


Figure 5 Molecular weight distributions for (A) poly[2-(4-vinylphenyl)ethyl acetate] initially polymerized, $\bar{M}_n$ obs. (v.p.o.) = 57 000, and (B) poly[α-methylstyrene-*b*-2-(4-vinylphenyl)ethyl acetate-*b*-α-methylstyrene]

Table 6 Block copolymerization of **4a** with styrene or α-methylstyrene with lithium naphthalide in THF at −78°C

			Block copolymer[a]			
			Calculated values		Observed values[b]	
Type	A monomer	B monomer	$\bar{M}_n$	[A]/[B]	$\bar{M}_n$	[A]/[B]
A–B–A	**4a**	Styrene	41 000	40/60	39 000	43/57
A–B–A	**4a**	α-Methylstyrene	52 000	41/59	53 000	49/51

[a] Yields: 98–100%; $\bar{M}_w/\bar{M}_n$: 1.10–1.15; deprotected and acetylated
[b] Determined by v.p.o. and ^{1}H n.m.r.

such restrictions that the monomer **4a** must not be polymerized first, since the living anion of poly(**4a**) is not sufficiently stable.

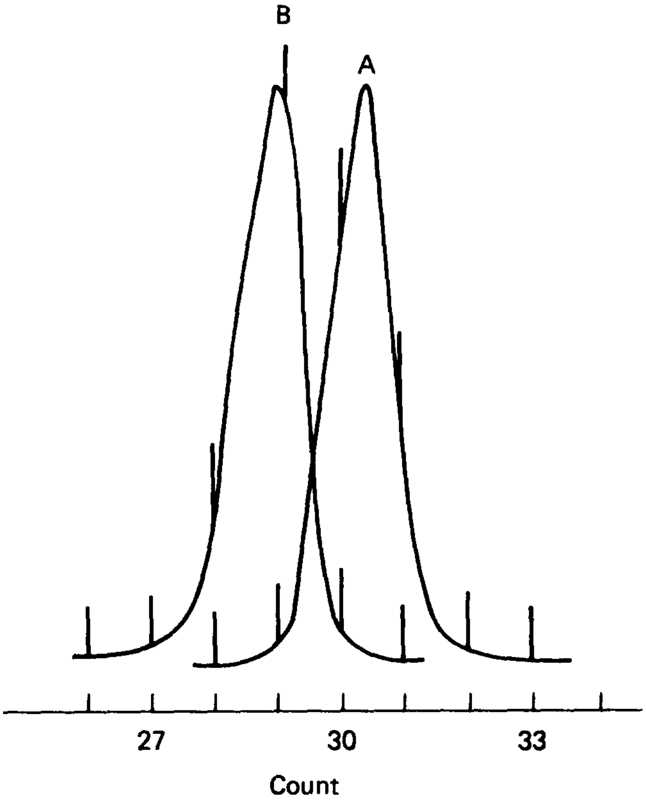


Figure 6 Molecular weight distributions for (A) poly(α-methylstyrene) initially polymerized, $\bar{M}_n$ obs. (v.p.o.) = 28 000, and (B) poly[2-(4-vinylphenyl)ethyl acetate-*b*-α-methylstyrene-*b*-2-(4-vinylphenyl)ethyl acetate], $\bar{M}_n$ obs. (v.p.o.) = 53 000 (see *Table 6*)

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