

## **Polymeric reagents: preparation and characterization of novel solid-phase silylating agents derived from copolymers containing 4-[3'-(dimethyl phenyl silyl)-propyl]-styrene**

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### Summary

Two novel reactive polymers useful as protecting groups for hydroxyls have been prepared by copolymerization of a silicon containing monomer, 4-[3'-(dimethyl phenyl silyl)-propyl]-styrene, with styrene and divinylbenzene, followed by chemical modification of the resulting insoluble polymer beads. The polymeric reagents containing trialkylsilyl chloride or trialkylsilyl trifluoroacetate moieties are effective for the protection of alcohols and a procedure for their facile regeneration is described.

### Introduction

The protection of hydroxyl groups by catalyzed silylation with hindered silylchlorides remains an important tool in synthetic organic chemistry [1]. This report describes the preparation of two polymeric silylating reagents, containing respectively trialkyl silyl chloride and trialkyl silyl trifluoroacetate functionalities. Incorporated into lightly crosslinked polystyrene gels, these silylating groups should allow for facile protection and separation of alcohols. All reaction steps, including the eventual chemical modification of the polymer-protected alcohol and the final deprotection reaction, can be expected to benefit from the insolubility of the polymeric protecting group [2]. The use of polymers as reagents [3] or protecting groups [4] in organic synthesis has been reviewed.

The polymeric reagents were prepared as insoluble spherical beads by suspension copolymerization of 4-[3'-(dimethyl phenyl silyl)-propyl]-styrene (24 mole %), with styrene (71 mole %) and commercial divinylbenzene (2.5 mole % divinylbenzene and 2.5 mole % ethylstyrene). Subsequent displacement of the phenyl group, using either thionyl chloride with a trace of water [5], or trifluoroacetic acid/anhydride, gave the corresponding reactive polymers with the structure shown below.

The design of these reagents is such that silicon is anchored to the polymer through an aliphatic three carbon spacer that is stable to the conditions used in the various steps of alcohol protection, cleavage, and regeneration of the silylating agents.

While numerous reactive polymers are prepared by chemical modification of chloromethylated polystyrene [6], usually through a simple nucleophilic displacement of chloride, this has sometimes resulted in complications due to the special reactivity of the resulting benzylic moieties. The use of two or three carbon spacer groups between the aromatic rings of the styrenic resins and the reactive moieties has been advocated earlier [7] and has led to more stable structures and frequently more predictable reactivities in the resulting polymeric reagents or catalysts [8].

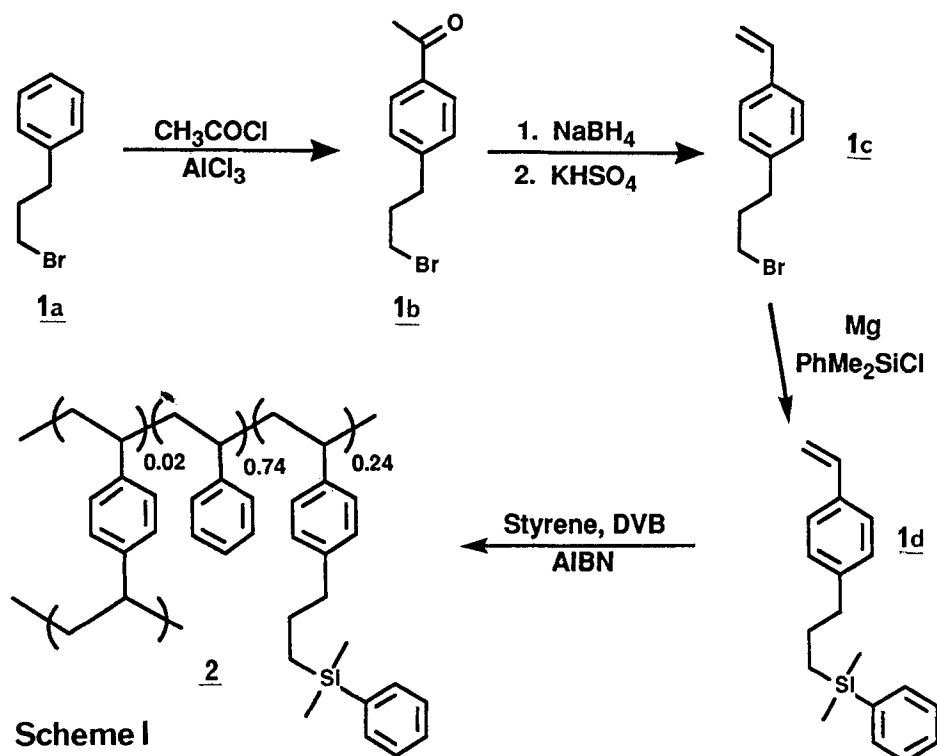
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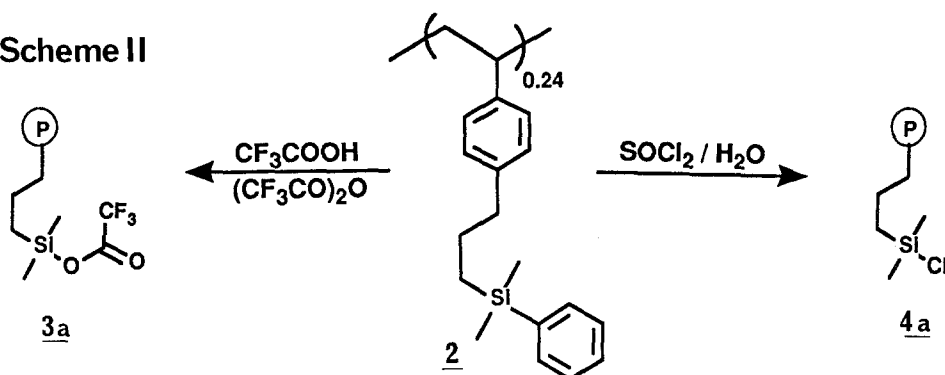
### Results and Discussion

The preparation of crosslinked polymer **2**, the precursor common to both silylating reagents **3a** and **4a** is shown in Scheme I. The percentage of each comonomer was chosen to provide a final polymer with a degree of functionalization (DF) of about 0.24. The silicon containing monomer itself, **1d**, was obtained in three steps from (3-bromopropyl)benzene. Acetylation [9] of (3-bromopropyl)benzene **1a** occurs predominantly in the para position to give 4-(3-bromopropyl)-acetophenone, **1b**. Subsequent reduction [10] and dehydration [11] produces the 4-(3-bromopropyl)-styrene **1c**. Finally, Grignard reaction [12] of **1c** with dimethylphenylchlorosilane affords the desired monomer **1d**. Suspension-copolymerization of **1d** under standard conditions [3, 13] with styrene as comonomer, and divinylbenzene as crosslinking agent affords the silicon containing bead polymer **2** (Scheme I).



The polymeric trialkylsilyl group in **2** constitutes an excellent leaving group with respect to the phenyl group attached to silicon. In a version of electrophilic aromatic substitution called protodesilylation, this silyl group can be displaced by the appropriate acid proton to produce benzene besides the desired polymeric silyl chloride or silyl trifluoroacetate [14, 15]. These reactions which afford the desired polymeric reagents **3a** and **4a** are shown in Scheme II.

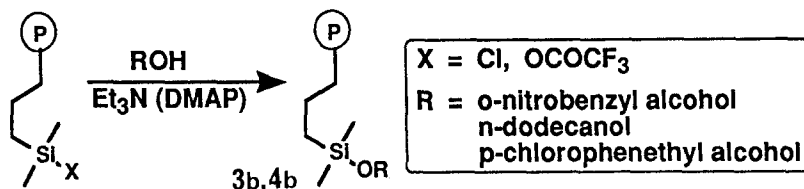
## Scheme II



Therefore, treatment of **2** with a mixture of trifluoroacetic acid and trifluoroacetic anhydride (7:1 w/w) at  $35^\circ\text{C}$  for 60-70 hours, followed by washing with  $\text{CCl}_4$  and drying under vacuum gave the polymeric silyl-trifluoroacetate reagent **3a** in essentially quantitative yield. Similarly, the polymer-bound silyl chloride reagent **4a** is readily obtained by treating **2** with thionyl chloride in the presence of a trace amount of water.

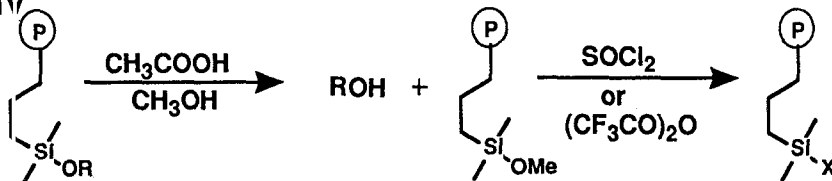
The procedure for the protection of alcohols using **3a** or **4a** is shown in Scheme III. With both reagents, coupling to an alcohol is best accomplished in the presence of an excess of tertiary amine, usually triethylamine, acting as an acid acceptor. The addition of a catalytic amount of DMAP (5 mole%) facilitates the coupling step. Typical reactions afford the polymeric silyl ethers **3b**, **4b** in coupling yields of 52-84% based on the silicon contents of the starting polymers. The actual coupling yields may in fact be significantly higher as not all of the silicon present in the polymeric reagent may be in the required reactive form.

## Scheme III



Cleavage of the polymeric silyl ethers (Scheme IV) is accomplished in quantitative yield using acetic acid in methanol. This liberates the free alcohol in solution while the polymeric by-product is a mixture of the silyl ether and acetate **3c**, **4c**. Finally the polymeric reagents can be regenerated using either thionyl chloride, to give the polymeric silyl chloride **4a** or using trifluoroacetic anhydride to give the corresponding silyl trifluoroacetates **3a**. The regenerated polymers were both used repeatedly in the same protection-deprotection-regeneration cycle. The results obtained in these reactions with various alcohols are reported in Table 1.

## Scheme IV



For the polymeric silyl trifluoroacetates **3a**, only approximately 52% to 63% of the silicon content appears to be in a reactive form. The polymeric silylchloride reagent **4a** by comparison appears to have a higher reactivity with 77-85% of the Si containing sites active. These degrees of activity remain constant through four successive reaction cycles with

intermediate regenerations, and the polymer capacity does not appear to depend on the nature of the alcohol used. The lower silylating capacity of the polymeric trifluoroacetates may be due either to incomplete displacement of the phenyl or methoxy groups by the trifluoroacetic acid, or to incomplete reaction with alcohol. This assumption is supported by an experiment in which a sample of a polymeric trifluoroacetate **3a** used previously in the protection of an alcohol, then deprotected (entry #5 in Table 1) was successfully regenerated with thionyl chloride to give a highly reactive polymeric silylchloride **4a** (entry #11 in Table 1).

Another possible, if perhaps minor, factor for the differences in reactivity of **3a** and **4a** may be the different reaction temperatures used in reactions of the trifluoroacetate polymer (as compared to those of the silylchloride polymer) both with alcohol (40°C versus 50°C) and during regeneration (35°C versus 40°C).

TABLE 1. Use of polymers **3a** and **4a** in the protection of alcohols.

Exp. #	Polymer	DF	Cycle	Alcohol <sup>c</sup>	Base	Capacity <sup>d</sup> (mmole/g)	% Activity <sup>e</sup>
1	<b>3a</b>	0.24 <sup>a</sup>	1	N	Et <sub>3</sub> N	0.74	53
2	<b>3a</b>	0.24 <sup>a</sup>	2	N	Et <sub>3</sub> N	0.86	62
3	<b>3a</b>	0.24 <sup>a</sup>	3	C	Et <sub>3</sub> N	0.72	52
4	<b>3a</b>	0.24 <sup>a</sup>	4	N	Et <sub>3</sub> N	0.87	63
5	<b>3a</b>	0.24 <sup>a</sup>	1	N	Et <sub>3</sub> N	0.80	60
6	<b>3a</b>	0.24 <sup>a</sup>	2	D	Et <sub>3</sub> N/DMAP	0.83	62
7	<b>4a</b>	0.22 <sup>b</sup>	1	D	Et <sub>3</sub> N	1.04	80
8	<b>4a</b>	0.22 <sup>b</sup>	2	D	Et <sub>3</sub> N	0.98	77
9	<b>4a</b>	0.23 <sup>b</sup>	3	D	Et <sub>3</sub> N/DMAP	1.07	80
10	<b>4a</b>	0.22 <sup>b</sup>	4	D	(i-pr) <sub>2</sub> EtN	1.10	84
11 <sup>f</sup>	<b>4a</b>	0.22 <sup>b</sup>	3	N	Et <sub>3</sub> N/DMAP	1.13	85

<sup>a</sup> Degree of functionalization estimated from initial Si content of polymer **2**

<sup>b</sup> DF of polymers **4a** was calculated from the chloride content of the polymer.

<sup>c</sup> Alcohol used: N = o-nitrobenzyl alcohol; C = p-chlorophenethyl alcohol; D = 1-dodecanol

<sup>d</sup> Capacity calculated from the amount of alcohol recovered after cleavage.

<sup>e</sup> % Activity calculated from capacity and DF values.

<sup>f</sup> The polymer (**4a**) used in #11 was regenerated from that used in Exp #5 (**3a**).

### Characterization of the Polymers

All polymeric products were characterized by <sup>13</sup>C-NMR of the polymer swollen in deuteriochloroform. In the resulting gels, the linear chain segments are well solvated and thus have enough local mobility to afford reasonably well resolved spectra of the aliphatic region [16]. In addition to the usual chemical shift information thus obtainable, the linewidths can provide clues regarding the effective degree of crosslinking. Errede and Newmark, in fact, recently demonstrated the correlation between <sup>13</sup>C-linewidths and crosslink densities for a series of solvent swollen polystyrene gels [17]. In a related area, our recent work [18] on the NMR characterization of solvent swollen gels of the type used in this report has also shown the versatility of direct polarization magic angle spinning (DP/MAS) techniques for the full characterization of lightly crosslinked polystyrene resins.

These results will appear elsewhere [19].

The functional groups most relevant for the characterization of our polymers are the different dimethylsilyl units. They are attached to the polymer backbone through a flexible trimethylene spacer, and are thus rather flexible in the solvent swollen gel. We found the silylmethyls to be sensitive  $^{13}\text{C}$ -NMR probes for reaction at the silicon center.

The quantitative displacement of phenyl by chloride in the formation of **4a**, for example, was verified by the almost complete absence of the phenyl dimethyl silane signal (-2.93ppm) in the spectrum of **4a**. Instead, there appeared an equally intense signal at +1.9ppm, characteristic of the dimethyl chlorosilyl group of **4a**. After reaction with alcohol, the dimethyl silyl signal shifts again to high field (-1.9ppm) in agreement with the formation of the silyl-ether **4b**. Deprotection with acetic acid/methanol leads to formation of a mixture of polymeric silyl products, as reflected by a number of dimethyl silyl signals between +0.5 and -2.2ppm. These products include mainly the methoxysilyl ether (-2.2ppm) besides some silyl acetate and disiloxane (~0.4ppm).

Regeneration with thionyl chloride is almost complete as indicated by the reappearance of a dominant signal for the dimethylsilyl chloride moiety (-1.9ppm).

In addition to the dimethyl silyl group and its propyl carrier, the protected ethers **4b** show well resolved  $^{13}\text{C}$  signals, with linewidths decreasing with the distance from the polymer backbone.

All  $^{13}\text{C}$ -NMR spectra of the polymeric trifluoroacetates **3a** and their product polymers showed larger linewidths than the corresponding polymers of the silyl chloride series (**4a**). This suggests either insufficient swelling of the matrix in deuteriochloroform, or more likely, the presence of siloxane crosslinks that are not cleaved by the trifluoroacetic anhydride. Either of these phenomena would reduce the accessibility of the interior to the alcohol as well as to any reagent used for deprotection or regeneration. In agreement with this, the  $^{13}\text{C}$ -NMR spectra of the trifluoroacetate series **3a-3c** while generally confirming the expected chemical modifications, indicated incomplete regeneration with trifluoroacetic anhydride.

### Conclusion

The polymeric silylating reagents **3a** and **4a** described in this report have good potential for use as polymeric protecting groups [4,5]. The loading data and well as spectroscopic evidence obtained by  $^{13}\text{C}$ -NMR support each other to suggest that, of the two reagents, the chlorosilane **4a** is superior to the trifluoroacetate **3a** and is therefore the reagent of choice. The design we have selected offers sufficient stability to experimental conditions to allow for repeated use in successive protection-deprotection-regeneration cycles.

The  $^{13}\text{C}$ -NMR data in particular indicate that the trifluoroacetate system is limited largely by incomplete regeneration rather than by incomplete reaction with the alcohol.

### Experimental

Styrene, divinylbenzene (50% solution in ethylvinylbenzene, Fluka AG) were distilled prior to use. O-Nitrobenzyl alcohol was recrystallized from chloroform and 1-dodecanol was distilled from calcium oxide. Triethylamine and diisopropylethylamine were distilled from calcium carbide. All solvents were dried. Infrared spectra were measured on a Nicolet 10-DX FT-IR spectrometer. NMR spectra were recorded on a Varian XL-300 spectrometer. Mass spectra were obtained on a VG-7070E using direct probe or chemical ionization. Elemental analyses were performed by MHW Laboratories and Galbraith Laboratories.

### Synthesis

*4-(3-bromopropyl)-acetophenone 1b.*

Compound **1b** was prepared in 79% yield from (3-bromopropyl)benzene **1a** using the acetylation procedure described by Foreman et al.<sup>5</sup> b.p.: 109°C (0.08 mm Hg). M.S.: m/e 240, 242 (M+); 225, 227.  $^1\text{H}$ -NMR:  $\delta$  (PPM) 2.17 (m, 2H) 2.57 (s, 3H) 2.83 (t, 2H) 3.37 (t, 2H) 7.26 and 7.86 (2d, phenyl, 4H).

*4-(3-bromopropyl)styrene 1c.*

Compound **1b** was reduced to the corresponding alcohol in quantitative yield using the sodium borohydride procedure described by Snider.<sup>6</sup> M.S.: m/e 242, 244 (M+); 227, 229; 149. <sup>1</sup>H-NMR:  $\delta$  (PPM) 1.47 (d, 3H) 2.15 (m, 2H) 2.76 (t, 2H) 3.38 (t, 2H) 4.86 (q, 1H) 7.15-7.30 (2d, phenyl, 4H).

Dehydration with potassium hydrogen sulfate according to the procedure of Overberger et al.<sup>7</sup> gave the desired styrene derivative **1c** in 87% yield. b.p.: 84.5°C (0.08 mm Hg) M.S.: m/e 224, 226 (M+); 117. <sup>1</sup>H-NMR:  $\delta$  (PPM) 2.14 (M, 2H) 2.75 (t, 2H) 3.38 (t, 2H) 5.17-5.21 (dd, 1H) 5.67-5.73 (dd, 1H) 7.13-7.16 and 7.31-7.34 (dd, 4H).

*4-(3-dimethylphenylsilyl)-propyl-styrene 1d.*

Monomer **1d** was obtained by a Grignard reaction similar to that reported by Pike<sup>8</sup>. The Grignard reagent was prepared from chlorophenyldimethyl silane and magnesium in dry THF. The reaction afforded the crude silicon-containing monomer which was then purified by column chromatography on silica using hexane as eluent, the yield of pure **1d** was 67.5% while a slightly impure fraction containing an additional 13% of **1d** was also obtained. M.S.: m/e 281; 203; 135. <sup>1</sup>H-NMR:  $\delta$  (PPM) 0.24 (s, 6H) 0.77 (m, 2H) 1.61 (m, 2H) 2.58 (t, 2H) 5.15, 5.19 (dd 1H); 5.65, 5.71 (dd, 1H); 6.63-6.72 (dd, 1H); 7.07-7.33 (Phenyl, 4H); 7.33-7.48 (Phenyl, 5H).

*Suspension copolymerization of 4-(3'-dimethylphenylsilyl)-propyl-styrene with styrene and divinylbenzene. Preparation of 2 with DF = 0.24.*

The suspension copolymerization was carried out in a Büchi BEP 280 autoclave using a 250ml vessel with anchor type stirrer using the procedure of Rolls et al. [12]. To 80mL of a 1.5% degassed solution of poly(vinyl alcohol) (Polyviol W25/40 Wacker Chemie) in distilled water was added a mixture of 12.1g monomers containing ca. 24 mole% of **1d** (5.6g **1d**; 6.0g styrene and 0.6g of 50% divinylbenzene solution in ethylvinylbenzene) in 18g toluene containing 0.2g of azobisisobutyronitrile, while stirring at 330 RPM. Nitrogen was bubbled through the mixture for 10 minutes. The polymerization was started by heating the suspension system to 80°C, and continued for 19 hours. The resulting polymer beads were decanted and washed with water until the supernatant stayed clear. Finally, the polymer beads were washed repeatedly with methanol and benzene, and dried in vacuo at 40°C to afford 10.1g of bead polymer **2** (83%). Analysis (MHW): (C; H; Si) % calculated: 87.22; 8.12; 4.66. Found: 87.30; 8.06; (4.64% Si by difference). Another sample prepared under similar conditions, with a slightly smaller percentage of divinylbenzene in the monomer feed (5.6g **1d**; 6.0g styrene and 0.5g of 50% divinylbenzene solution in ethylvinylbenzene), afforded polymer **2** in somewhat lower yield and having the following elemental analysis (Galbraith): found; C, 87.30; H, 8.40, Si, 5.50 (total: 101.2%).

IR: 1426 and 1112cm<sup>-1</sup> (Si-Ar) 1248 and 881cm<sup>-1</sup> (Si-aliphatic)

<sup>13</sup>C-NMR:  $\delta$  (PPM) -2.93 (Si-CH<sub>3</sub>) 15.75 (Si-CH<sub>2</sub>-) 25.97 (Si-CH<sub>2</sub>-CH<sub>2</sub>-) 39.47 (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-) 40.37 (CH, backbone) 40-48 (CH<sub>2</sub>, backbone) 125.141-144.6 (aromatic, backbone + pendant phenyl). The carbon multiplicities were verified using the DEPT pulse sequence.

*Polymeric n-propyldimethylsilyl trifluoroacetate 3a.*

2.0030g of bead polymer **2** was placed in a flask and 4g of trifluoroacetic acid and 2g of trifluoroacetic anhydride were added. The mixture was stirred for 60-70 hours at 35°C. Then the beads were filtered, washed with CCl<sub>4</sub> under N<sub>2</sub> and dried in vacuo at 40°C for 24 hours to afford 2.1044g of polymer **3a**. The IR spectrum of **3a** showed absorption bands at 1768, 1220, and 1169cm<sup>-1</sup> (from trifluoroacetate). The bands at 1426 and 1112cm<sup>-1</sup>, characteristic of the Si-Ar band, are absent. <sup>13</sup>C-NMR:  $\delta$  (PPM) -2.1 (CH<sub>3</sub>) 15.57 (SiCH<sub>2</sub>) 26.83 (Si-CH<sub>2</sub>-CH<sub>2</sub>) 39.5 (Si-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>) 40.33 (CH, backbone) 40-46 (CH<sub>2</sub>, backbone) 128.25 (phenyl) 160.3 (c=O).

*Polymeric n-propyldimethylsilyl chloride 4a.*

2.0736g of bead polymer **2** were placed in a 50mL flask with 25g of thionyl chloride.

After stirring to swell the polymer beads, 0.06ml of water was injected by microsyringe. The reaction was allowed to proceed at 40°C for 70 hours. Then the polymer beads were filtered and washed with  $\text{CCl}_4$  under  $\text{N}_2$ , and dried in vacuo for 24 hours at 45°C. 1.9108g of polymer **4a** was obtained. Chlorine analysis indicated a chloride content of 1.6 meq/g resin. The  $^{13}\text{C}$ -NMR spectrum also showed about 3% unreacted phenyl silyl groups. IR: peaks at 1426 and  $1113\text{cm}^{-1}$  have disappeared, peak at  $881\text{cm}^{-1}$  of Si-alkyl has shifted to  $846\text{cm}^{-1}$ , and a new peak at  $467\text{cm}^{-1}$  (Si-Cl bond) is seen.  $^{13}\text{C}$ -NMR:  $\delta$  (PPM) +1.83 (Si- $\text{CH}_3$ ) 18.87 (Si- $\text{CH}_2$ -) 25.07 (Si- $\text{CH}_2\text{CH}_2$ -) 38.83 (Si- $\text{CH}_2\text{CH}_2\text{CH}_2$ -) 40.38 (CH, backbone) 40.48 ( $\text{CH}_2$ , backbone) 124.67-144.99 (aromatic).

#### Testing of the polymeric silylating reagents for protection of simple alcohols.

##### (a) Formation of polymer-bound silyl ether **3b** from polymeric *n*-propyldimethylsilyl trifluoroacetate **3a**.

1.4832g of polymer **3a** was added to a mixture of 0.49g (3.2mmol) of *o*-nitrobenzyl alcohol and 0.34g (3.2mmol) of triethylamine in 5mL of dichloroethane. The reaction mixture was left for 48 hours at 40°C. The polymer was then filtered (some losses occurred) and washed with  $\text{CH}_2\text{Cl}_2$  until no *o*-nitrobenzyl alcohol was detected, and dried in vacuo at 40°C to afford 1.3859g of polymer **3b** was obtained. The nitrogen content of polymer **3b** was found to be 1.04%, corresponding to an alcohol loading of 0.74 mmol/g. Silicon elemental analysis showed 4.11% suggesting that only 53% of the silicon containing sites were used in the coupling of the alcohol. IR: bands at 1768, 1220 and  $1169\text{cm}^{-1}$  disappeared, new bands at 1525 and  $1339\text{cm}^{-1}$  (aromatic  $\text{NO}_2$ ) are seen.  $^{13}\text{C}$ -NMR:  $\delta$  (PPM) -2.11 (Si- $\text{CH}_3$ ) 15.99 (Si- $\text{CH}_2$ ) 25.12 (Si- $\text{CH}_2\text{CH}_2$ ) 39.50 (Si- $\text{CH}_2\text{CH}_2\text{CH}_2$ ) 40.34 (CH, backbone) 42-46 ( $\text{CH}_2$ , backbone) 61.54 (-O- $\text{CH}_2$ -) 124.50-147.3 (aromatic).

##### (b) Cleavage of polymer-bound silyl ether **3b** and recovery of the alcohol.

1.125 g of Polymer **3b** was added to a mixture of 4.0g methanol and 0.15g acetic acid. The mixture was stirred for 36 hours at room temperature. After filtration, the polymer was washed repeatedly with  $\text{CH}_2\text{Cl}_2$  and methanol. The filtrate and washings were combined and the solvents evaporated. The residue was purified by silica gel column using ethyl acetate as eluent. A white crystalline product was obtained and dried in vacuo at 30°C for 2 hours. 0.1247g of crystalline material and 0.9937g of polymer **3c** were obtained. The white crystals were identified as *o*-nitrobenzyl alcohol by IR and  $^1\text{H}$ -NMR. The recovered polymer **3c** contained 4.71% silicon, a value well within experimental errors for the expected reaction sequence. IR spectra of polymer **3c** show no absorption at 1525 and  $1339\text{cm}^{-1}$  from the nitro group. The broad NMR lines indicate that additional crosslinking through formation of disiloxane links had occurred.  $^{13}\text{C}$ -NMR:  $\delta$  (PPM) -2.49 (Si $\text{CH}_3$ ) 15.83 (Si $\text{CH}_2\text{CH}_2$ ) 25.29 (Si $\text{CH}_2\text{CH}_2\text{CH}_2$ ) 40.26 (CH) 50.19 (SiO $\text{CH}_3$ ) 127.87 (phenyl).

##### (c) Regeneration of polymeric *n*-propyldimethylsilyl trifluoroacetate **3a**.

4g of trifluoroacetic anhydride was added to a flask charged with 0.8846g of polymer **3c**. The reaction mixture was stirred for 49 hours at 35°C, then filtered and washed using dry  $\text{CCl}_4$  under  $\text{N}_2$  and dried in vacuo at 40°C. 1.0137g of polymer **3a** was obtained. IR spectra showed the presence of the expected peaks at 1768; 1220 and  $1169\text{cm}^{-1}$ .  $^{13}\text{C}$ -NMR:  $\delta$  (PPM) -2.21 (Si $\text{CH}_3$ ) 15.17 (Si- $\text{CH}_2$ ) 26.97 or 24.4 (Si- $\text{CH}_2\text{CH}_2$ ) 39.5 (Si- $\text{CH}_2\text{CH}_2\text{CH}_2$ ) 40.33 (CH, backbone) 42-46 ( $\text{CH}_2$ , backbone) 114 ( $\text{CF}_3$ ) 128 (phenyl) 156 (C=O).

##### (d) Formation of polymer-bound silyl ether **4b** from polymeric *n*-propyldimethylsilyl chloride **4a**.

To a solution of 2.51g (13.5 mmol) 1-dodecanol and 1.33g (13.5 mmol) triethylamine in 8mL dichloroethane was added 1.6766g of polymer **4a**. The reaction mixture was stirred for 46 hours at 50°C. After filtration, polymer **4b** was washed with  $\text{CH}_2\text{Cl}_2$  5 times during 2 hours, and dried in vacuo at 40°C to afford 1.9755g of polymer **4b**. IR: disappearance of peak at  $467\text{cm}^{-1}$  (Si-Cl); new peak at  $1089\text{cm}^{-1}$  (Si-OR).  $^{13}\text{C}$ -NMR:  $\delta$  (PPM) -1.86 (Si- $\text{CH}_3$ ) 14.28 ( $\text{CH}_3$ , alcohol) 16.51 (Si- $\text{CH}_2$ -) 22.79 ( $\text{CH}_2$ , alcohol) 25.44 (Si- $\text{CH}_2\text{CH}_2$ ) 25.94 ( $\text{CH}_2$ , alcohol) 29.44-29.73 (7  $\text{CH}_2$ , alcohol) 32.00 ( $\text{CH}_2$ , alcohol) 32.88 ( $\text{CH}_2$ ,

alcohol) 39.5 (Si-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-) 62.83 (CH<sub>2</sub>, alcohol) 40.46 (CH, backbone) 40-45 (CH<sub>2</sub>, backbone) 127.72 (phenyl).

*(e) Cleavage of polymer-bound silyl ether 4b and recovery of the alcohol.*

1.0706g of polymer **4b** was added to a solution of 4g methanol and 0.15g of acetic acid. The mixture was stirred for 36 hours at room temperature. The polymer was then filtered and washed repeatedly using CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>OH. The filtrate and washings were combined, and the solvents evaporated. The residue was purified by column chromatography over silica gel using ethyl acetate as eluent. The recovered alcohol was identified as 1-dodecanol (0.2091g) while 0.8591g of polymer **4c** was also recovered after drying in vacuo. <sup>13</sup>C-NMR: δ (PPM) -2.15 (Si-CH<sub>3</sub>) 18.04 (Si-CH<sub>2</sub>-) 25.59 (Si-CH<sub>2</sub>CH<sub>2</sub>-) 39.68 (Si-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-) 40.59 (CH, backbone) 40-48 (CH<sub>2</sub>, backbone) 50.44 (Si-O-CH<sub>3</sub>) 127-96-142.55 (phenyl). Here again, the broad NMR lines indicate that additional crosslinking through formation of disiloxane links had occurred.

*(f) Regeneration of polymeric n-propyldimethylsilyl chloride 4a.*

1.3978g of polymer **4c** was stirred with 8g thionyl chloride for 48 hours at 40°C under nitrogen. The polymer was then filtered and washed with CCl<sub>4</sub> under N<sub>2</sub>, dried in vacuo at 45°C for 24 hours. 1.4434g of polymer (**4a**) was obtained. The chloride content of polymer **4a** was 1.59meq/g. IR: appearance of peak at 467cm<sup>-1</sup>. <sup>13</sup>C-NMR: δ (PPM) 1.89 (Si-CH<sub>3</sub>) 18.94 (Si-CH<sub>2</sub>-) 25.12 (Si-CH<sub>2</sub>CH<sub>2</sub>-) 38.83 (Si-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-) 40.43 (CH, backbone) 40-48 (CH<sub>2</sub>, backbone) 125.59-145.06 (phenyl).

**Acknowledgements.**

Financial support of this research by a gift of IBM corporation and by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged. Thanks are also due to Dr. G.D. Darling for stimulating discussions on spacer modified reactive polymers.

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