



Functional transformation of poly(dialkylaminotrimethyldisilene) prepared by anionic polymerization of the masked disilenes. The preparation of a true polysilastyrene

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Abstract

The Si–N bond of the amino-substituted polysilane, poly[1,1,2-trimethyl-2-(dibutylamino)disilene] yields chloro-substituted polysilanes. Substitution with some nucleophiles, such as a Grignard reagent, organolithium reagents, hydrides, and alcohols, yields a new class of polysilanes. This synthetic route provides a true polysilastyrene with a head-to-tail structure.

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1. Introduction

Polysilanes [1] have attracted considerable interest during the last decade because of their interesting electronic and photophysical properties, and their potential application in the field of materials, such as being ceramic precursors [2], as electrical conductors [3], in photoconductivity [4], in microlithography [5], and as nonlinear optical devices [6]. The unusual properties of polysilanes are extremely sensitive to the conformation of the polymers and to the substituents attached to the polymer backbone. In this respect, heteroatom-substituted polysilanes should prove very interesting because of their anticipated properties. However, most common synthetic methods employed to prepare polysilanes, e.g.

the Wurtz coupling of dichlorosilanes with alkali metals, limits the potential routes for introducing functional organic groups into polysilanes. Although some recent successes have been noted with substitution reactions onto polysilane chains, such as use of a selective free radical of poly(phenylsilane) [7] and the dearylation of poly(phenylmethylsilane) [8], these reactions did not proceed with regioselectivity, and were still limited. Recently, there have been reports of some heteroatom-substituted polysilanes [9].

Anionic polymerization of masked disilenes presents an exciting opportunity for the synthesis of polysilanes with a well-defined structure that would otherwise be very difficult to prepare [10]. Indeed, we have found that amino-substituted masked disilenes can be prepared and polymerized successfully to form unprecedented amino-substituted polysilanes with a completely head-to-tail structure, poly[1,1,2-trimethyl-2-(dibutylamino)disilene] [11]. This polysilane is interesting not only because of the effect of the amino groups on the electronic properties of the main chain, but also because of the substitution of an amino group followed by its subsequent

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reaction with nucleophiles. Because the chlorination of an amino group on the silicon usually proceeds smoothly to give a chlorination product [12], the Si–N bond of amino-substituted polysilanes affords chloro-substituted polysilanes with a head-to-tail structure for use as starting materials to synthesize new polysilanes. In this paper, we report on the regioselective substitution of amino-substituted polysilanes as a synthetic route to a new class of polysilanes.

2. Results and discussion

2.1. Preparation of amino-substituted polysilanes

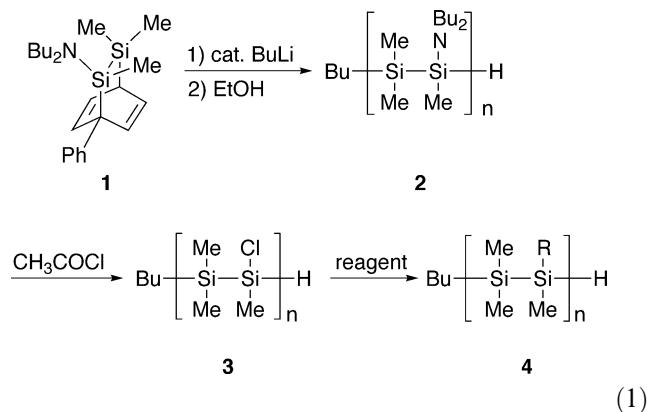
Recently, we have found that amino-substituted masked-disilenes can be prepared and polymerized successfully to form amino-substituted polysilanes with an alternating structure, poly[1,1,2-trimethyl-2-(dialkylamino)disilene] [11]. The required masked disilene **1** was prepared by a reaction of 1,1,2-trimethyl-2-(dialkylamino)-1,2-dichlorodisilane with a biphenyl anion radical. Rather surprisingly, a high regioselectivity of the reaction was observed. Only one of the possible regioisomers was obtained. Previous results have shown that the isomer ratio obtained depended on the steric bulkiness of the group substituted on silicon. However, such a complete regioselectivity has never been observed before [13]. For the amino-substituted derivative, the regioselectivity was amplified not only by the steric bulkiness, but also by the electronic effect of the amino group.

The anionic polymerization of the masked disilenes in THF with a catalytic amount of *n*-butyllithium gave the amino-substituted polysilanes in a high yield (see Eq. 1). The polymerization process itself was regioselective in a sterically head-to-tail fashion. Indeed, the ¹H-, ¹³C-, and ²⁹Si-NMR spectra showed that the structure of the polymer had a completely head-to-tail structure, poly[1,1,2-trimethyl-2-(dibutylamino)disilene], as has been previously reported [11].

2.2. Preparation of chloro-substituted polysilanes

The reaction of the amino-substituted polysilane and acetyl chloride at room temperature yielded poly(1,1,2-trimethyl-2-chlorodisilene) in a high yield as a slightly soluble white powder. Although the exact structure of the polymer was not determined because of the very low solubility, elemental analysis showed that the obtained polysilane did not contain any nitrogen atoms, and that the general structure was confirmed by solid-state NMR spectra. Only two signals were observed in the CP-MAS ²⁹Si-NMR, occurring at –33.3 and 16.6 ppm. The reaction of poly[1,2-dimethyl-1-butyl-2-(dibutylami-

no)disilene] with acetyl chloride was attempted, which yielded a slightly soluble chloro-substituted polysilane, the structure of which was confirmed by NMR spectroscopy.



2.3. Reaction of chloro-substituted polysilane with some nucleophiles

The substitution of the Si–Cl bonds of the polymer was examined for a variety of nucleophiles (see Eq. 1 and Table 1). For example, the alkylation of the chloro-substituted polysilane with butylmagnesium bromide was carried out. Although the chloro-substituted polysilanes were insoluble in the solvents used, the reaction proceeded smoothly, and poly(1,1,2-trimethyl-2-butyl-disilene) was obtained in a high yield. Gel permeation chromatography (GPC) measurements demonstrated that the molecular weight of the obtained polymer agreed very closely with the calculated values of an amino-substituted polysilane. This indicated that no degradation of the main chain occurred in the reaction. Further NMR analysis supported the proposed structure of the polymer. In the ¹H- and ¹³C-NMR spectra, peaks ascribed to butyl groups on the polymer were observed, while the peaks ascribed to the dibutylamino groups on the amino-substituted polysilanes completely disappeared. Fig. 1 shows the dimethylsilylene region of the ¹³C-NMR spectrum of the polymer. Two sharp peaks assignable to the head-to-tail structure of the –SiMe₂– and –BuSiMe– units were observed for the polysilane prepared from the chloro-substituted polysilane. Fig. 1 also shows the ¹³C-NMR spectrum of a polysilane prepared by anionic polymerization of 1,1,2-trimethyl-2-butyl-substituted masked disilenes, which has a mixture of a regioisomers in a 6:4 ratio (Eq. 2) [13]. The polysilane showed four peaks assigned to the methyl group of the head-to-tail and head-to-head structures. This marked difference supports the proposition that the polymer prepared from the chloro-substituted polysilane has a high head-to-tail regulated

Table 1
Substitution of amino groups on side-chain of the polysilanes

Run	Reagent	Yield/%	M_n^a (obs.)	M_n^b (calc.)	M_w/M_n
1	BuMgBr	91	22 000	24 000	2.4
2	PhLi	78	15 000	22 000	2.2
3	^c AllMgCl	45	8800	7900	2.4
4	BuOH/Et ₃ N	52	33 000	27 000	1.9

^a Determined by GPC with polystyrene standards.

^b Based on the amino-substituted polysilanes.

^c All, allyl (2-propenyl).

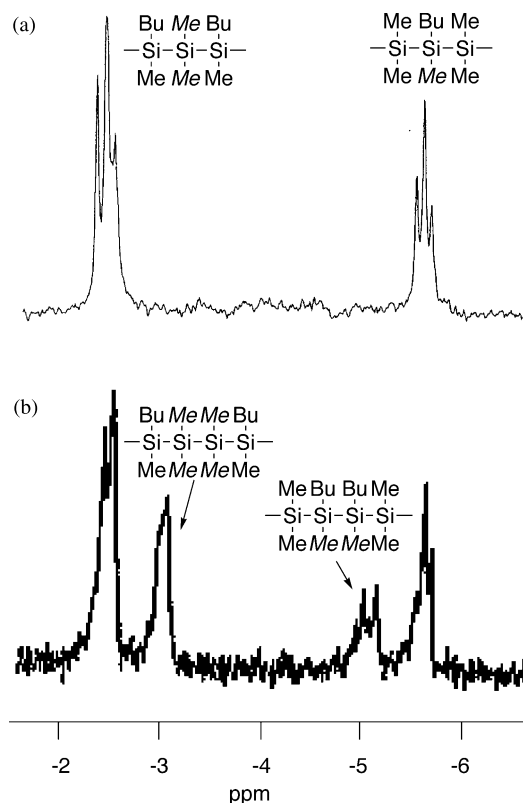
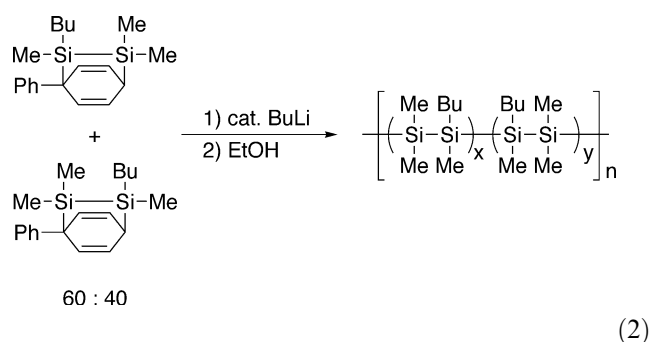


Fig. 1. The dimethylsilylene region of ¹³C-NMR spectrum of (a) the polymer prepared from the chloro-substituted polysilane and (b) a polysilane prepared by anionic polymerization of 1,1,2-trimethyl-2-butyl-substituted masked disilenes (a mixture of a regioisomers in a 6:4 ratio).

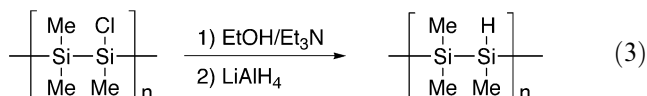
structure. In the NMR spectrum of the polymer, very small splittings were observed in each peak. Since the sequence regularity of the polymer is very high, these small splittings are not ascribable to the irregular structure of the main chain, but to the main chain tacticity. The ²⁹Si-NMR spectrum was consistent with that of a polymer chain with a highly regulated head-to-tail structure: only two signals at -36.58 and -32.58 ppm were observed. Again, this polymer had a highly regulated head-to-tail structure. These results suggest that a regioselective substitution reaction had occurred.



This synthetic strategy has allowed us to synthesize a real head-to-tail polysilastylene. In 1981, West et al. reported the first synthesis of a soluble polysilane copolymer from methylphenyldichlorosilane and dimethyldichlorosilane [14]. The copolymer was called polysilastylene, based on its structural similarity to a similar carbon-based polymer, i.e., polystyrene. However, the structure of the copolymer was block-like, containing runs of the respective monomer units, and hence the polymer was not truly 'polysilastylene' [15]. Our synthetic strategy provides a method for synthesizing polysilastylene with a head-to-tail structure, because the amino-substituted polysilane has a sequence with a completely head-to-tail structure, and the ensuing substitution reactions proceed in a regioselective manner. Considering these advantages, the synthesis of a polysilastylene with head-to-tail structure was examined. The reaction of the chloro-substituted polysilane with phenyllithium also gave poly(1,1,2-trimethyl-2-phenyldisilene) in a good yield (Run 2 in Table 1), and the structure of the obtained polymer was confirmed using GPC and NMR. We have now succeeded in the preparation of the real head-to-tail polysilastylene polymer about 20 years after the first synthesis of a soluble polysilane.

The substitution of some functional groups on the chloro-substituted polysilanes was also examined. Allylation of the chloro-substituted polysilanes with allylmagnesium chloride produced allyl-substituted polysilane in a good to reasonable yield (Run 3 in Table 1). An alcohol can be substituted into the polymer backbone under mild conditions in the presence of triethylamine to yield alkoxy-substituted polysilanes

(Run 4 in Table 1). The synthesis of H-substituted polysilanes was also examined. Unfortunately, the reduction of the chloro-substituted polysilane with lithium aluminum hydride did not yield a high molecular weight polymer, but the reduction of ethoxy-substituted polysilanes with lithium aluminum hydride afforded H-substituted polysilanes without any degradation of the main chain (yield = 62%, $M_n(\text{obs.}) = 8400$, $M_n(\text{calc.}) = 5300$, see Eq. 3).



The procedure is a simple method for synthesizing polysilanes with a special structure having functional groups that is otherwise very difficult to prepare. Further work is now in progress.

3. Experimental

3.1. General procedure

All the reactions were carried out under a highly purified argon atmosphere in a VAC glove box. The ^1H -, ^{13}C -, and ^{29}Si -NMR spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer at frequencies of 300, 75.4, and 59.6 MHz, respectively. The ^1H and ^{13}C chemical shifts were relative to an internal CHCl_3 standard. The ^{29}Si chemical shift was referenced to an external Me_4Si (0 ppm) standard. The GLC data was recorded on a Shimadzu GC-8A chromatograph. The molecular weight distributions of the polymers were measured using a Shimadzu LC 10 HPLC equipped with PL-gel mixed-C columns, and calibrated using polystyrene standards with THF as the eluent. The UV spectra were recorded on a Milton Roy Spectronic 3000 Array spectrometer. The THF, diethyl ether, and toluene were dried and distilled from a sodium/benzophenone mix just before their use. The hexane, butyl alcohol, and triethyl amine used were dried and distilled from calcium hydride just before use. The acetyl chloride used was distilled just before use. The phenyllithium (cyclohexane/diethyl ether solution) and lithium aluminum hydride were used without any further purification. The hexane used in the spectroscopic measurements was of commercial UV spectral grade, and was used without further purification.

3.2. Synthesis of poly[1,1,2-trimethyl-2-chlorodisilene]

Acetyl chloride (980 mg, 12.5 mmol) was added to a room temperature (r.t.) solution of poly[1,1,2-trimethyl-2-(dibutylamino)disilene] (375 mg, 1.64 mmol for disilene units) in hexane (20 ml). After the addition, the

reaction mixture was stirred for 30 min, and then, a white precipitate was found to have been deposited. Filtration from the solution, followed by removal of the solvent in a vacuum afforded the polymer as a white powder (190 mg, 85%). Spectral data: ^1H -NMR ($\text{THF-}d_8$, δ) 0.10–0.40 (bm, 6H), 0.50–0.80 (bm, 3H); Solid-state CP-MAS ^{29}Si -NMR (59.59 MHz, δ) –33.3, 16.6.

Poly[1,2-dimethyl-1-butyl-2-chlorodisilene] was prepared using the same procedure as above to yield slightly soluble chloro-substituted polysilane product. Spectral data: ^1H -NMR (CDCl_3 , δ) 0.52 (bs), 1.00 (bs), 1.52 (bs); ^{13}C -NMR (CDCl_3 , δ) –9.2, –6.5, 3.7, 5.0, 13.2, 14.0, 27.5, 29.5.

3.3. Synthesis of poly[1,1,2-trimethyl-2-butylidisilene]

The poly(1,1,2-trimethyl-2-chlorodisilene) (178 mg, 1.31 mmol for disilene units) and THF (20 ml) were placed in a 50 ml Schlenk flask, equipped with a magnetic stirring bar, under an argon atmosphere. An ether solution of *n*-butylmagnesium bromide (4.1 mmol), prepared from the reaction of 1-bromobutane (8.22 g, 60 mmol) and magnesium (1.64 g, 67 mmol), was added to the solution at r.t. The mixture was stirred for 40 h, and a few drops of ethanol were then added to the mixture. After removal of the solvent, the residual mass was dissolved in benzene, and the polymer precipitated by pouring the solution into acetone. A second dissolving-precipitation cycle followed by freeze-drying afforded the polymer as a white powder (187 mg, 91%, $M_n = 22\,000$, $M_w/M_n = 2.4$). Spectral data: ^1H -NMR (CDCl_3 , δ) 0.18 (bs, 3H), 0.22–0.27 (bm, 6H), 0.72–0.93 (bm, 6H), 1.31 (bs, 4H); ^{13}C -NMR (CDCl_3 , δ) –5.59, –5.52, –5.44 (BuMeSi), –2.42, –2.33, –2.25 (Me_2Si), 13.73, 14.10, 27.11, 29.09; ^{29}Si -NMR (CDCl_3 , δ) –36.58, –32.58; UV (hexane, r.t.) $\lambda_{\text{max}} = 305$ nm ($\epsilon_{(\text{Si-Si})} = 5000$).

3.4. Synthesis of poly[1,1,2-trimethyl-2-phenylidisilene]

Phenyllithium in cyclohexane-ether (2.06 mmol) was added to a benzene solution of poly(1,1,2-trimethyl-2-chlorodisilene) (197 mg, 1.44 mmol for disilene units) at r.t. The mixture was stirred for 5 h, and then a few drops of ethanol were added to the mixture. After removal of the solvent, the residual mass was dissolved in benzene, and the polymer precipitated by pouring the solution into acetone. A second dissolving-precipitation cycle followed by freeze-drying afforded the polymer as a white powder (200 mg, 78%, $M_n = 15\,000$, $M_w/M_n = 1.6$). Spectral data: ^1H -NMR (CDCl_3 , δ) –0.70–0.60 (bm, 12 H), 6.62–6.65 (bm, 5 H); ^{13}C -NMR (CDCl_3 , δ) –8.40, –7.82, –7.08 (PhMeSi), –3.20 to –2.30 (m, Me_2Si), 127.22, 134.30, 136.75–137.49 (m); ^{29}Si -NMR (CDCl_3 , δ) –38.4 to –36.3 (bm); UV (hexane, r.t.) $\lambda_{\text{max}} = 316$ nm ($\epsilon_{(\text{Si-Si})} = 5400$).

3.5. Synthesis of poly[1,1,2-trimethyl-2-allyldisilene]

Allyl magnesium bromide (4.5 mmol), prepared from the reaction of allylchloride (4.56 g, 60 mmol) and magnesium (1.62 g, 68 mmol) in THF, was added to an ether solution of poly(1,1,2-trimethyl-2-chlorodisilene) (216 mg, 1.58 mmol for disilene units) at r.t. The mixture was stirred for 40 h, and then a few drops of ethanol were added to the mixture. After removal of the solvent, the residual mass was dissolved in benzene, and the polymer precipitated by pouring the solution into acetone. A second dissolving-precipitation cycle followed by freeze-drying afforded the polymer as a white powder (200 mg, 78%, $M_n = 8800$, $M_w/M_n = 2.4$). Spectral data: $^1\text{H-NMR}$ (CDCl_3 , δ) 0.20–0.47 (bm), 2.00–2.02 (bm), 5.00–5.11 (bm), 5.94–6.02(bm); $^{13}\text{C-NMR}$ (CDCl_3 , δ) –5.08, –2.19, –2.08, –1.95, –3.20, 21.78, 113.70, 136.42; $^{29}\text{Si-NMR}$ (CDCl_3 , δ) –38.4, –36.3; UV (hexane, r.t.) $\lambda_{\text{max}} = 295$ nm.

3.6. Synthesis of poly[1,1,2-trimethyl-2-butoxydisilene]

1-Butanol (320 mg, 3.20 mmol) and triethyl amine (250 mg, 3.40 mmol) were added to a benzene solution of poly(1,1,2-trimethyl-2-chlorodisilene) (150 mg, 1.10 mol for disilene units) at r.t., and the mixture stirred for 40 h. After filtration, a second dissolving-precipitation (benzene/acetone) cycle followed by freeze-drying afforded the polymer as a white powder (99 mg, 52%, $M_n = 33\,000$, $M_w/M_n = 1.9$). Spectral data: $^1\text{H-NMR}$ (CDCl_3 , δ) 0.47, 0.57, 0.67 (Me_2Si), 0.79, 0.82, 0.84 ((BuO)MeSi), 0.97 (3 H), 1.48 (2 H), 1.67 (2 H), 3.80 (2 H); $^{13}\text{C-NMR}$ (CDCl_3 , δ) –4.02, –3.65, –3.23 (Me_2Si), –0.23, –0.09, –0.06 ((BuO)MeSi), 14.25, 19.60, 35.67, 65.86; $^{29}\text{Si-NMR}$ (CDCl_3 , δ) –43.03 (Me_2Si), 17.37, 17.52 ((BuO)MeSi); UV (hexane, r.t.) $\lambda_{\text{max}} = 316$ nm ($\epsilon_{\text{Si-Si}} = 5200$).

3.7. Synthesis of poly[trimethyldisilene]

Ethanol (210 mg, 4.5 mmol) and triethyl amine (450 mg, 4.50 mmol) were added to a benzene solution of poly(1,1,2-trimethyl-2-chlorodisilene) (500 mg, 3.50 mol for disilene units) at r.t., and the mixture stirred for 40 h. After filtration and evaporation of the solvent, an ether solution of lithium aluminum hydride was added to the residue. The mixture was stirred for 90 h, and then, a few drops of water were added to the mixture. The organic layer was extracted with benzene. After this procedure, the polymer was precipitated after a second dissolving-precipitation cycle followed by freeze-drying, which afforded the polymer as a white powder (200 mg, 62%, $M_n = 8400$, $M_w/M_n = 1.8$). Spectral data: $^1\text{H-NMR}$ (C_6D_6 , δ) 0.25–0.47 (bm, 12H), 3.73 (bm 1H); $^{13}\text{C-NMR}$ (C_6D_6 , δ) –10.78, –10.71, –10.65, –3.34,

–2.75, –2.10; $^{29}\text{Si-NMR}$ (C_6D_6 , δ) –66.45, –66.31, –66.16, –37.86, –37.78, –37.71, –37.66, –37.59; UV (hexane, r.t.) $\lambda_{\text{max}} = 270$ nm ($\epsilon_{\text{Si-Si}} = 1500$).

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