



Chiral diamine catalyzed induction of helical chirality in polysilanes



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ABSTRACT

Controlling the conformation polysilane through proton-metal exchange reaction of polymethyltolylsilane with alkyllithium using catalytic amount of chiral amines as the chiral origin has been realized. The produced polymers whose chiral origins are (–)-sparteine, (S, S)-3 or (S)-2 adopt the P conformation, and whose chiral origins are (R, R)-3 or (R)-2 adopt the M conformation. Under the external stimuli of (S, S)-3 and (R, R)-3, or (S)-2 and (R)-2, the prepared polymers, PS-11 and PS-12 or PS-3 and PS-2 assumed to induced CD spectra were virtual mirror images of each other. These results indicate that the chiral amines can not only induce the helicity of polysilanes, but control the direction of the helix.

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Introduction

Much attention has been focused on the controlling synthesis and optical activity of chiral polysilanes or oligosilanes [1]. This is because such materials with one-handed screw-sense are useful as potential chiral selectors for recognition, amplification and catalysis, and especially for applications in the areas of micro-lithography, optical switches, and data storage [2]. These rod-like helical polysilanes possess unique electronic and photophysical properties compared to other optical active π -conjugated polymers, such as marked ultraviolet (UV), circular dichroism (CD), and fluorescence (FL) bands around 300–400 nm which originates from the σ -delocalization along the Si–Si bonds of the main chain. Because these properties are extremely sensitive to the backbone conformation, the optically active polysilanes are ideal models for the investigation of the relationship between their main chain conformational structures and inherent optical properties [3]. The optical activities reported in the literature so far are mainly induced by the incorporation of chiral pendants [4] or end groups [5], or by the stimuli of external agents such as complexing molecules [6] or chiral solvents [7]. However, to the best of our knowledge, using catalytic amount of chiral diamines to alter the equilibrium between two opposing helical senses in optically inactive polysilanes has not been investigated so far.

Using the complexes of chiral diamine ligands and organolithiums, such as (–)-sparteine ((–)-**sp**)-*n*-BuLi, (+)-(S)-1-(2-

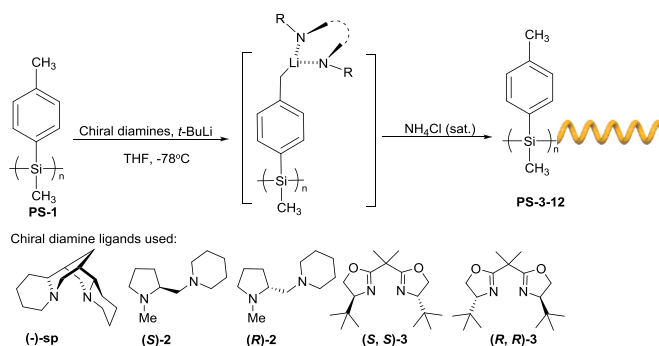
pyrrolidinylmethyl)pyrrolidine(PMP)-9-fluorenyllithium(FILi) and (S, S)-(+)-2,3-dimethoxy-1,4-bis(dimethylamino)butane ((+)-DDB)-9-fluorenyllithium(FILi) as chiral catalysts to induce the asymmetric polymerization, or anionic polymerization of designed bulky methacrylates and acrylates have been investigated widely [8]. These prepared polymers adopt a one-handed helical conformation, although they contain no chiral components. Lithiation of the pendant tolyl group of poly(4-methylstyrene) using alkyllithium to give the polymeric benzyllithium, is well studied in organic synthesis [9]. We anticipate that the metallation of polymethyltolylsilane with the complexes of alkyllithium and chiral diamine ligands may produce the polysilane intermediates having chiral pendants and the amplified chiral information of ligands could be transferred to the backbone of the Si-main chain to induce a preferential screw sense to the polymer main chain. After removal the chiral ligands by hydrolysis by using the saturated NH₄Cl, the produced polysilane will maintain the chiral information derived from the pendant group and therefore its optical activity (Scheme 1). With these thoughts in mind, firstly, we investigated the helicity of polymethyltolylsilane [10] induced by the (–)-**sp** complex of *t*-BuLi.

Results and discussion

When polymethyltolylsilane (**PS-1**) was treated with catalytic amount of (–)-**sp** (10 mol%) and *t*-BuLi (10 mol%) in THF at –78 °C for 0.5 h, after hydrolysis with saturated NH₄Cl, the produced polymer (**PS-5**) exhibited a strong positive Cotton band at 352 nm in the CD spectrum in the solid state (Table 1, entry 4). The **PS-5**

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Scheme 1. Chiral diamines – *t*-BuLi complex induced helical chirality of polymethyltolylsilane.

showed an absorption maximum at 339 nm, but did not show any CD signals in THF solution at room temperature, because the polymer has a random-coil conformation in solution. The absorption maximum of **PS-5** shifted from 339 to 352 nm in the solid state. This indicates that polysilane chain adopts a predominant *transoid* conformation derived from the restriction of the conformational mobility. The optical activity of **PS-5** must be attributed to the helicity of the rigid isotactic Si-backbone sequence induced by (–)-**sp** through the proton-metal exchange reaction of polymethyltolylsilane with the complexes of (–)-**sp-t-BuLi**. Because under similar reaction conditions, the polysilanes (**PS-2**, **PS-13**) derived from achiral ligand such as EDTA or without the ligand showed no optical activity at all (Table 1, entries 1 and 12). The intensity of the induced ICD increased with increasing the amount of (–)-**sp** used (entries 2–4). The basicity of alkyllithium is also a key factor for the induction of the helicity to the polysilane. When *n*-BuLi or lithium hexamethyldisilazide (LiHMDS) was used instead of *t*-BuLi in the presence of catalytic amount of (–)-**sp**, the produced **PS-7** and **PS-8** exhibited similar but weaker ICD signals than that of **PS-3-5** (entries 6 and 7). The main reason is that the basicity of *t*-BuLi is stronger than that of *n*-BuLi and LiHMDS, and the proton-metal exchange reactions of polymethyltolylsilane with *t*-BuLi is completely compare to *n*-BuLi and LiHMDS. Thus, for *t*-BuLi, the formation of helical polysilane complex **B** is easily (Scheme 2), and shows strong ICD signal. If (–)-**sp** was used without alkyllithium, no ICD signal was detected for the resulted polymer (**PS-6**, entry 5 in Table 1).

Table 1
Diamine ligands induced optical activity of polysilane ^a.

Entry	Diamine(equiv.)	Base(equiv.)	PS ^b	Sign ^c	$\Delta\epsilon/\text{cm}^{-1} \text{M}^{-1}$
1	–	<i>t</i> -Bu(100%)	PS-2	–	–
2	(–)- sp (100%)	<i>t</i> -Bu(100%)	PS-3	+	8.52
3	(–)- sp (50%)	<i>t</i> -Bu(50%)	PS-4	+	6.33
4	(–)- sp (10%)	<i>t</i> -Bu(10%)	PS-5	+	5.64
5	(–)- sp (10%)	–	PS-6	–	–
6	(–)- sp (10%)	<i>n</i> -Bu(10%)	PS-7	+	2.23
7	(–)- sp (10%)	LiHMDS(10%)	PS-8	+	2.12
8	(<i>S</i>)- 2 (10%)	<i>t</i> -Bu(10%)	PS-9	–	6.25
9	(<i>R</i>)- 2 (10%)	<i>t</i> -Bu(10%)	PS-10	+	5.89
10	(<i>S,S</i>)- 3 (10%)	<i>t</i> -Bu(10%)	PS-11	–	12.78
11	(<i>R,R</i>)- 3 (10%)	<i>t</i> -Bu(10%)	PS-12	+	11.69
12	TMEDA ^d	<i>t</i> -Bu(10%)	PS-13	–	–

^a Reaction conditions: Polymethyltolylsilane (1 mmol), alkyllithium (0.1–1 mmol), diamine ligands (0.1–1 mmol), THF (10 mL) at –78 °C.

^b Polysilanes were purified by the precipitation of its THF solution into MeOH.

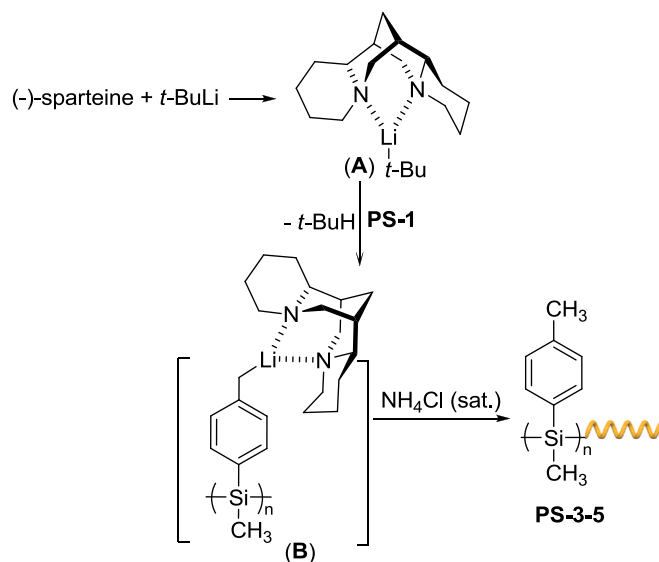
^c The UV and CD spectra were measured using KBr pellets (polysilane/KBr = 1/300, wt%).

^d Tetramethylethylenediamine.

Fig. 1 shows the CD and UV spectra of **PS-9** and **PS-10** which were derived from treating **PS-1** with the complexes of (*S*)-2-*t*-BuLi and (*R*)-2-*t*-BuLi, respectively. **PS-1** naturally shows no CD signal either in the molecularly dispersed solution or in the solid state. However, after lithiation with *t*-BuLi in the presence of catalytic amount of chiral diamine, (*S*)-2 or (*R*)-2, the distinct chirality-dependent CD signals were exhibited in the **PS-9** and **PS-10** (entries 8 and 9). No significant differences were visible among the UV–vis features of **PS-1**, **PS-9** and **PS-10**, that is, the chiral diamine ligands of (*S*)-2 and (*R*)-2 do not affect the electronic properties or the conformational preference of the silicon backbone. These results clearly indicate that chiral diamine ligands could not only induce the preferential screw sense of the polysilane but also control the helical direction. The origin of the induced CD effects would be ascribed to perturbing the balance of the helical screw senses of the silicon main-chain during the proton-metal exchange reaction of the polymethyltolylsilane with the (*S*)-2-*t*-BuLi or (*R*)-2-*t*-BuLi complex.

When (*S,S*)-**3** and (*R,R*)-**3** were used as chiral ligands under the similar reaction conditions as above, the produced polymers, **PS-11** and **PS-12**, show intensive Cotton bands at about 350 nm in the ICD spectra (entries 10 and 11) in the solid state at room temperature. The ICD spectra are virtually mirror images of each other, similarly to those of **PS-9** and **PS-10** [12]. These results indicate that **PS-11** and **PS-12** adopt a one-handed helical conformation, while the helicity is opposite to each other depending on the chiral stimuli, (*S,S*)-**3** or (*R,R*)-**3**.

It is likely that chiral diamine ligands such as (–)-**sp** reacts with *t*-BuLi to attain a complexation equilibrium as shown in Scheme 2. The proton-metal exchange reaction takes place between the (–)-**sp-t-BuLi** complex (**A**) and polymethyltolylsilane (**PS-1**) forming an optical active lithiated polymer with a new organolithium/(–)-**sp** complex (**B**). The formation of complex **B** with chiral centres should be the key step for the induction of the helicity to the polysilane chain. The point chirality of the diamines would be transferred and amplified to the Si–Si main chain, thus the lithiated polymer **B** features a preferential screw sense. After hydrolysis of **B**, the chain helicity of the complex **B** is kept. That is, the produced polymer which contained no chiral components but had a chirality caused only by the helicity. As shown in Table 1, the catalytic amount of chiral diamine could induce and control the helical



Scheme 2. The mechanism for the induction of the helicity to the polysilane.

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