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Effect of the Chiral Center Position of an Optically Active Terminal Group on the Induction of Optical Activity in Polysilanes

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Summary

Polysilanes with an optically active alkoxy group, *i.e.*, (*S*)-(+)-2-butoxy, (*R*)-(−)-2-butoxy, (*S*)-(−)-2-methyl-1-butoxy, and (*S*)-(+)-3,7-dimethyl-1-octoxy, at the terminal positions, the chiral carbon centers of which were located at the α, β, and γ positions relative to the oxygen, respectively, were prepared, and the effect of the position of chiral center of the terminal optically active group on the induction of optical activity in polysilanes was investigated. The circular dichroism (CD) spectra of these polymers showed positive Cotton signals around 340 nm at temperatures below –20 °C, but the intensities were small, indicating that the optically active groups at the terminal positions have some ability, albeit small, to induce optical activity to the polysilanes. Further, the optically active (*S*)-(+)-2-butoxy and (*R*)-(−)-2-butoxy groups did not control the helical sense direction of the polymers, despite the different chiral stimuli from the 2-butoxy groups introduced to the terminal positions. To control the helical structure of polysilanes by the use of optically active terminal groups, appropriate optically active groups are required.

Introduction

Control of the helical structure of polymers or oligomers has been the subject of intense study recently. This is because such materials with controlled structures could be useful as potential chiral selectors for separation and catalysis, and especially as chiroptical materials for switching and in memory devices [1]. Helical structures are often found in biomacromolecules like DNA and proteins and appear to play critical roles in biological phenomena such as molecular recognition and information storage, for example. Some synthetic polymers also adopt a helical conformation, even in solution. New approaches to synthesizing polymers with helical conformation have been used by various researchers [2].

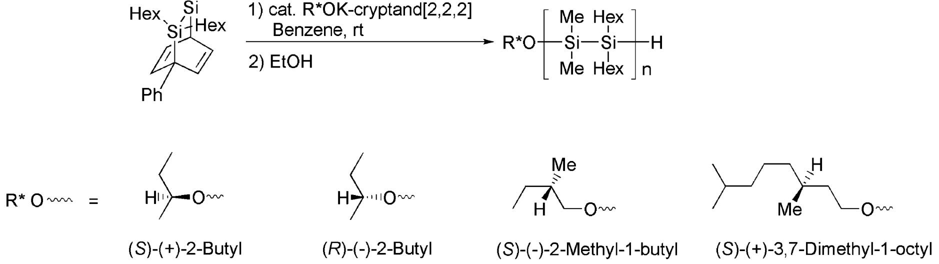
Among the synthetic polymers with helical structures, polysilanes are particularly interesting because of their unique electronic and photophysical properties. The unique properties are attributed to the σ-conjugation occurring along the main chain, and hence the extreme sensitivity to the polymer conformation [3]. Polysilanes, which can induce a preferential helical conformation when substituted with optically active side chains [4] or end groups [5], allow us to study the relationship between the photophysical properties and the conformation of the polymer main chain. Recently we reported on helical-sense programming in a polysilane-poly(triphenylmethyl methacrylate) block copolymer [6]. In this system the polysilane main chain in the block copolymer was induced to form a preferential helical conformation by the helix conformation of the poly(triphenylmethyl methacrylate) block.

We have also studied the polymerization of masked disilenes initiated by alkoxides [7]. Among the advantages of using alkoxides as an initiator is the ease with which they introduce an optically active group to the end of a polymer chain. We found that when initiated with optically active (+)- or (−)-menthoxide, the polymer has the optically active group at the terminal position, and then adopts a preferential helical-sense conformation in solution at low temperature and also in the solid state at room temperature [8]. Because the optically active terminal group induces optical activity in the polysilane in this system, the position of the chiral centers on the optically active terminal group should be important. In this paper we describe the effect of the position of the chiral center of the terminal optically active group on the induction of optical activity in polysilanes.

Results and Discussion

Synthesis of polysilanes with an optically active terminal group

The polymerization of masked disilenes initiated by potassium alkoxides in the presence of cryptand [2.2.2] in benzene proceeds smoothly, especially when using potassium (−)- or (+)-menthoxide [7]. Polysilanes with an optically active terminal group were prepared by the anionic polymerization of masked disilenes, initiated by optically active alkoxides, which were easily prepared by the reaction of the corresponding alcohols and potassium. To acquire polysilanes possessing a chiral center at the terminal position, the polymerization of masked disilenes, initiated by potassium (*S*)-(+)-2-butoxide, (*R*)-(−)-2-butoxide, (*S*)-(−)-2-methyl-1-butoxide, and (*S*)-(+)-3,7-dimethyl-1-octoxide was examined, as shown in Scheme 1. The initiator has a chiral carbon center at the α, β, and γ positions relative to the alkoxy oxygen.



1a **1b** **2** **3**

Scheme 1

Table 1. Polymerization Data for Anionic Polymerization of Masked Disilene Initiated by Optically Active Alkoxides[a]

Run	Initiator: R*-OK (mol%)	Polymer	Yield (%)	*M*n[b]	*M*w/*M*n[b]	DP[c]
1	(*S*)-(+)-2-butoxyK (5)	**1a**	26	6500	1.3	25
2	(*R*)-(−)-2-butoxyK (5)	**1b**	16	6100	1.3	24
3	(*S*)-(−)-2-methyl-1-butoxyK (5)	**2**	35	6700	1.3	26
4	(*S*)-(+)-3,7-dimethyl-1-octoxyK (5)	**3**	40	6700	1.3	26

[a] Polymerization conditions: room temperature, 15 s. [b] Estimated using GPC with polystyrene standards (eluent: THF). [c] Degree of polymerization.

The results of the polymerization are summarized in Table 1. The molecular weights of the obtained polysilanes were measured by gel permeation chromatography (GPC), using polystyrene standards. For example, the polymerization initiated with 5 mol% potassium (*S*)-(+)-2-butoxide gave polymer **1a** in a 26% yield, with a number-averaged molecular weight of 6.5×10^3 (*M*w/*M*n = 1.3). The polymerization with potassium (*R*)-(−)-2-butoxide gave polymer **1b**, the molecular weight of which was *M*n = 6100. When using potassium (*S*)-(+)-3,7-dimethyl-1-octoxide and (*S*)-(+)-3,7-dimethyl-1-octoxide, polymers **2** and **3** were obtained, respectively. Both had molecular weights of 6700 and degrees of polymerization (DP) of 26. Polymers **1–3** had almost the same molecular weights and degrees of polymerization, hence this can rule out the effect of the molecular weight dependence on the photophysical properties, as shown below [8].

UV and CD measurements

Polysilanes with a long alkyl side chain usually exhibit unique UV spectra, resulting from their conformational changes [9]. Under the situation, the polysilane can chose to adopt a preferential one-handed helix conformation induced by the optically active group [8]. We found that the polymers with the optically active menthoxy group at the terminal position adopt a preferential helical sense conformation in solution at low temperature. The (+)- or (−)-menthoxy group, however, has three chiral carbon centers at the α, β, and γ positions, and hence it is not clear whether a particular chiral center or all the chiral centers can induce the optical activity in the polysilane.

To examine the effect of the position of chiral center on the terminal optically active group on the induction of optical activity in polysilanes, temperature dependent UV and CD measurements of polymers **1–3** were made. Figure 1 shows the temperature dependent UV and CD spectra of **1b**, as an example. Table 2 summarizes the photophysical data of **1–3** along with the data from the polymers **4** with an optically active menthoxy group at the terminal positions. Polymer **1b** showed an absorption maximum at 310 nm at room temperature in isooctane. However, at temperatures below –20 °C the absorption maxima shifted to 340 nm. The spectroscopic features are almost the same as previously observed for polymer **4** [8]. At room temperature the main chain assumes a random-coil conformation, while at low temperature the main chain assumes a predominant *transoid* conformation, where the dihedral angle is about 160–175° [10]. Figure 1 also shows the temperature dependent CD spectra of the polymer. Although no CD signal was observed at room temperature, as the temperature decreased to below –20 °C a positive CD signal was observed at 340 nm.

The intensity of the CD signal increased with decreasing temperature. The temperature at which the CD band appeared was similar to the transition temperature in the UV absorption spectra. This clearly indicates that the optically active terminal group induces the polysilane main chain to assume a preferential one-handed helical sense, to exhibit the optical activity under this set of experimental conditions. However, the molar circular diachronic extremum (Δε) for polymer **1b** was 0.49, which is much smaller than that observed for polymers **4a** and **4b**. This indicates that the (*R*)-(−)-2-butoxy group at the terminal position can induce optical activity in the polymer, but to a lesser extent than the optically active menthoxy group.

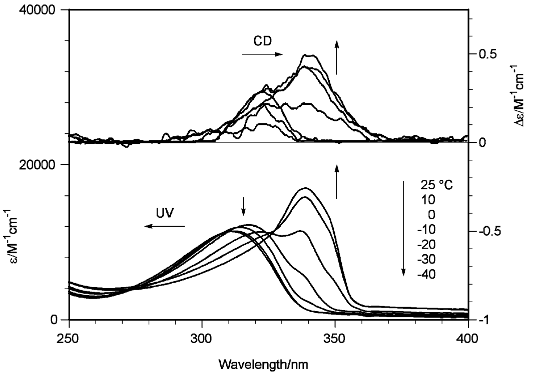


Figure 1. Temperature dependent UV and CD spectra of **1b** in isooctane.

Table 2. Data for the Optically Active Polysilanes in Isooctane at –40 °C

Polymer	R*O-	λmax / nm	Δε / $cm^{-1}M^{-1}$
1a	(*S*)-(+)-2-butoxy	347	0.62
1b	(*R*)-(−)-2-butoxy	344	0.49
2	(*S*)-(−)-2-methyl-1-butoxy-	345	0.52
3	(*S*)-(−)-3,7-dimethyl-1-octoxy-	340	0.72
4a[a,b]	(+)-menthoxy	348, 332	−1.68, 1.97
4b[a,c]	(−)-menthoxy	348, 332	3.07, −1.16

[a] Reference 8. [b] *M*n = 6800 (*M*w/*M*n = 1.3). [c] *M*n = 7200 (*M*w/*M*n = 1.3).

As reported previously, **4a** and **4b** with optically active (+)- or (−)-menthoxy groups at the terminal positions showed CD signals that had opposite signs [8], indicating that the polysilanes adopt a helical conformation, but in opposite directions in the helical sense as a result of different chiral stimuli from (+)- or (−)-menthoxy groups at the polymer end. However, a striking result was observed for **1**. Figure 2 shows the CD spectra of **1a** and **1b** at –40 °C in isooctane. Polymer **1a** with a (*S*)-(+)-2-butoxy group at the

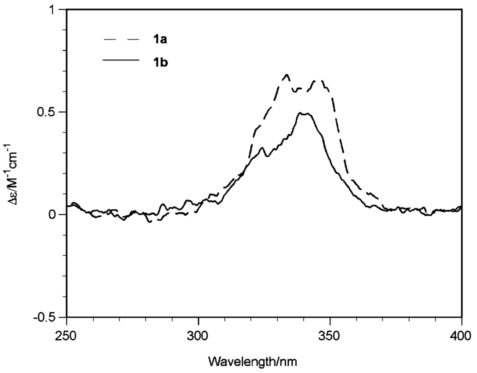


Figure 2. CD spectra of **1a** (broken line) and **1b** (solid line) at –40 °C in isooctane.

polymer end showed a positive CD signal at −40 °C, which is the same CD sign as observed for polymer **1b** with a (*R*)-(−)-2-butoxy group. This means that the optically active (*S*)-(+)- and (*R*)-(−)-2-butoxy groups induce the optical activity in the polymers, but no longer control the helical sense direction of the polymers [11].

The helical induction was also observed in films of **1a** and **1b** (Figure 3). The samples for UV and CD measurements were prepared by coating a solution of the polymer in benzene onto a quartz substrate, followed by evaporation. The UV spectrum of polymer **1a**, even at room temperature, showed an absorption maximum at 335 nm, where the polysilane chain assumes a predominant *transoid* conformation, probably due to the restriction of the conformational mobility. The CD spectrum of **1a** showed a positive Cotton signal at about 340 nm. The polymer with the opposite optically active group at the terminal position, **1b**, also showed a positive Cotton signal. Again, this means that the polysilane adopts a helical conformation, but the direction in the helical-sense is not controlled.

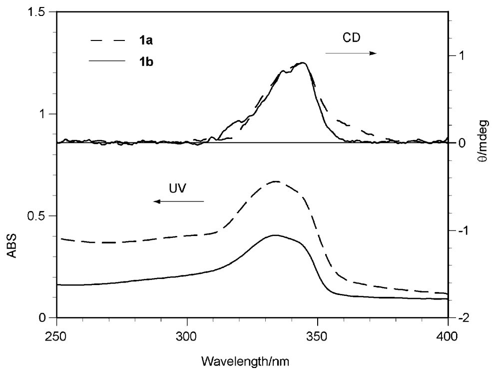


Figure 3. UV and CD spectra of films of **1a** (broken line) and **1b** (solid line) at room temperature.

Polymers **2** and **3** have the chiral carbon at the β and γ positions relative to the oxygen atom at the terminal position, respectively. In the temperature dependent UV spectra in isooctane, polymers **2** and **3** displayed almost the same spectral features as mentioned above; the absorption maxima shifted from 310 nm to 340 nm at temperatures below –20 °C. In the CD spectra, positive Cotton signals occurred at around 340 nm at temperatures below –20 °C for both polymers **2** and **3**. Table 2 shows the data of the CD spectra of **2** and **3** at –40 °C in isooctane. The intensities of the CD signals were weak compared to that of polymer **4**. As mentioned above, optically active (*S*)-(−)-2-methyl-1-butyl and (*S*)-(+)-3,7-dimethyl-1-octyl groups also induce optical activity in the polymer, but not to a large extent.

Conclusion

We prepared polysilanes with an optically active alkoxy group at the terminal positions, the chiral carbon centers of which were located at the α, β, and γ positions relative to the oxygen, respectively. The CD spectra of these polymers showed positive Cotton signals around 340 nm at temperatures below –20 °C in solution, but the intensities were much smaller than those observed for the polysilanes with (+)- or (−)-menthoxy groups at the polymer ends, indicating that the optically active group at the terminal position has some ability, albeit small, to induce optical activity to the polysilanes. In addition, the optically active 2-butoxy group did not control the helical sense direction of the polymers. To control the helical structure of polysilanes by the use of an optically active terminal group, appropriate optically active groups are required. The results reported here might be useful for the improved synthesis of optically active polysilanes.

Experimental Section

General

The data of the ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX 300 FT-NMR spectrometer at 300, 75.4, and 59.6 MHz, respectively. The ^{1}H and ^{13}C chemical shifts were referenced to solvent residues (^{1}H, $\delta = 7.24$ ppm, ^{13}C, $\delta = 77.0$ ppm for $CDCl_3$). The ^{29}Si chemical shifts were referenced to external Me_4Si (0 ppm). The GLC data were recorded on a Shimadzu GC-8A chromatograph. The molecular weight distributions of the polymers were measured by using a Shimadzu LC 10 HPLC equipped with PL-gel mixed-C columns calibrated with polystyrene standards. Tetrahydrofuran (THF) was used as an eluent. The UV spectra were recorded using an HP Agilent 8453 spectrometer. The CD spectra were obtained on a JASCO J-820 spectrometer.

Materials

All starting materials were obtained from commercial suppliers and were used as received. Benzene was dried over sodium/benzophenone and distilled under argon. The solvents were distilled again onto sodium under high vacuum immediately prior to use. The isooctane used for the spectroscopic measurements was of commercial UV spectral grade, and was used without further purification. 1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (masked disilene) was synthesized as described previously [7]. All the reactions were carried out under an argon atmosphere.

Synthesis of polymers

A typical example of a polymerization is as follows. The masked disilene (0.94 g, 2.29 mmol), cryptand [2.2.2] (48 mg, 0.127 mmol), and benzene (10 ml) were placed in a 50-ml two-necked flask under dry argon. A toluene solution of potassium (*S*)-(+)-2-butoxide (0.12 mmol), prepared from the reaction of potassium and (*S*)-(+)-2-butyl alcohol in toluene, was added to the solution at room temperature. The mixture was stirred for a period of 15 s, and then a few drops of ethanol were added to the mixture. After removal of the solvent, the residual mass was dissolved in benzene. The polymer was precipitated by pouring the solution into acetone. A second cycle of dissolving and precipitation, followed by freeze-drying, yielded **1a** as a white powder (150 mg, 26%), with $M\text{n} = 6.5 \times 10^{3}$, and $M\text{w}/M\text{n} = 1.3$, as determined using GPC with polystyrene standards. THF was used as an eluent: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.84–1.26 (m), 0.30 (brs); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ −0.66, 13.5, 14.1, 22.83, 31.7, 34.3; ^{29}Si NMR ($CDCl_3$, 59 MHz) δ −27.5, −35.9.

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11. Because Kira and coworkers reported control of the optical activity of oligo- and polysilanes with optically active 2-phenylpropyl groups at both terminal positions [5], the size of the optically active end group or two optically active end groups at both the terminal positions may be important to control the optical activity of polysilanes.