

The Induction of a Helical Conformation in Polysilanes with an Optically Active Terminal Group

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Polysilanes with an optically active terminal (+) or (−)-menthoxy group, prepared by the anionic polymerization of masked disilene, adopt a preferential helical-sense conformation in solution at low temperature and also in the solid state at room temperature. The dependence on the molecular weight of the helical induction is also discussed. In a good/poor mixed solvent system, the induction of a helical conformation in the polysilanes was observed when forming aggregates.

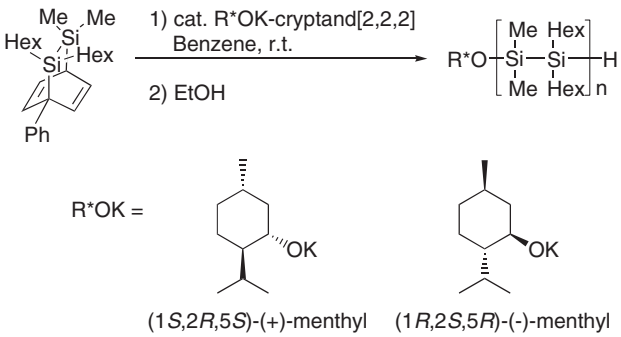
The control of the helical structure of macromolecules has been the subject of intense study recently, because these polymers could be useful as potential chiral selectors for separation and catalysis, and especially as chiroptical materials for switching and in memory devices. Some approaches to synthesizing polymers with helical conformations have been carried out.[1] One approach is the direct polymerization of chiral monomers. Another approach is the polymerization of achiral monomers using a chiral initiator with or without the presence of a chiral ligand (helix-sense-selective polymerization) to produce handed optically active polymers under predominantly kinetic control. A further example is provided by the non-covalent interaction of the polymer with optically active molecules.[2]

Polysilanes can also adopt a preferential helical-sense conformation when substituted with optical active side chains[3] or end groups,[4] and these allow us to study the photophysical properties in connection with the conformation of the polymer main chain. Recently, we reported on helical-sense programming in the polysilane–poly(triphenylmethyl methacrylate) block copolymer system.[5] 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).

We also investigated the polymerization of a masked disilene initiated by potassium alkoxides in the presence of cryptand 222 in benzene, which proceeded as a growth-initiated reaction, especially in the presence of potassium menthoxide.[6] Among the advantages of using alkoxides as initiators is their ease in introducing optically active groups to the ends of the polymer chains. These polymers then have the chance to adopt a preferential helical-sense conformation based on the application of an external stimulus. In this work, we report on the helical-sense programming in polysilanes with an optical active group at the terminal position.

Results and Discussion

Optically Active Alkoxide Initiation of Anionic Polymerization of Masked Disilenes to Polysilanes. Recently, we found the polymerization of a masked disilene initiated by potassium alkoxides in the presence of cryptand 222 in benzene proceeded, especially when using potassium (−)-menthoxide.[6] Polysilanes with an optical active terminal group were prepared by the anionic polymerization of masked disilene initiated by potassium (+) or (−)-menthoxide in the presence of cryptand 222 in benzene (Scheme 1). The results of the polymerization are summarized in Table 1. Polysilanes with a variety of molecular weights were obtained, with the molecular weights of the polymers ranging from 6800 to 20000 for the polymerization with both potassium (+) and (−)-menthoxide initiators. The molecular weight of the polysilanes obtained from GPC was in good agreement with the molecular weight estimated by the ^{1}H NMR analysis based on the integration ratio of the menthoxy group at the polymer end to the dimethylsilylene unit.



Scheme 1.

Thermochromic Behavior of Polysilanes with an Optically Active Terminal Group. Polysilanes with a long alkyl side chain usually exhibit unique electronic spectra depending upon their conformation, which changes with the environment, particularly temperature.[7] It is interesting that the polymers have an optically active group at the polymer ends. The temperature dependent UV behavior provided information on the conformation of the polysilane main chain. For example, the polysilane

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Table 1. Polymerization and Spectroscopic Data for Polysilanes with an Optically Active Terminal Group

Run	Initiator	M_n[a]	PDI[b]	UV[c]	CD[c]			
				λ_{max}/nm	First Cotton		Second Cotton	
				(ε)	Sign	$\Delta\varepsilon_1$ (λ_{ext}/nm)	Sign	$\Delta\varepsilon_2$ (λ_{ext}/nm)
1	(+)-Menthoxy	6800 (6700)[d]	1.3	336 (19000)	−	1.68 (348)	+	1.97 (332)
2		10000	1.3		−	2.62 (348)	+	2.97 (332)
3		14000	1.4		−	0.91 (348)	+	1.49 (335)
4		19000	1.4	336 (21000)	−	0.50 (350)	+	1.43 (336)
5	(−)-Menthoxy	7200 (7100)	1.3	337 (20000)	+	3.07 (348)	−	1.16 (332)
6		11000	1.4		+	1.76 (347)	−	0.32 (333)
7		15000	1.4		+	1.49 (348)	−	0.10 (330)
8		20000	1.4	336 (21000)	+	1.43 (348)	−	0.20 (330)

a) Estimated by GPC with polystyrene standards (eluent: THF). b) Polydipersity index (M_w/M_n). c) At −40 °C in isooctane. d) Obtained from ^{1}H NMR analysis.

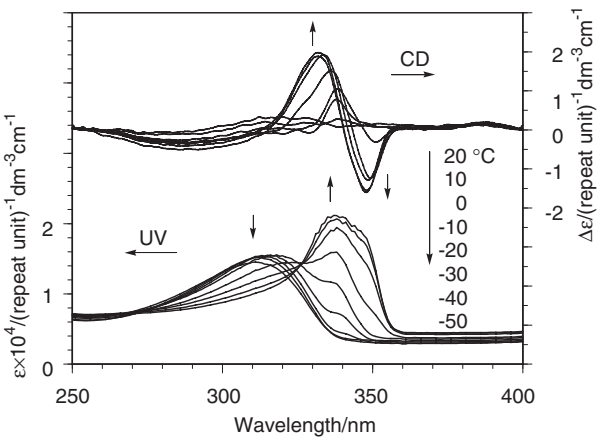

Fig. 1. Temperature dependent UV and CD spectra of polysilanes with a (+)-menthoxy group at the polymer end in isooctane ($M_n = 6800$).

with a molecular weight of 6800 showed an absorption wavelength maximum at $\lambda = 310$ nm at room temperature in isooctane (Fig. 1). However, at temperatures below −20 °C, the absorption maxima shifted to a wavelength of $\lambda = 340$ nm. The spectroscopic features are almost the same as previously observed for a polysilane without the optically active terminal groups.[8] The absorption maxima showed no shift for the polymers with the molecular weights ranging from 6800 to 20000.[9] This spectral change can be explained by a conformational change in the main chain, although the overall behavior of the transition is not obvious. 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 around 160–175°.[10]

Induction of Preferential One-Handed Helix Conformation in Polysilanes with an Optically Active Terminal Group in Solution. The polysilanes with an optically active terminal group exhibited a unique UV spectra resulting from their conformational change. Under this set of conditions, the polysilane can chose to adopt a preferential one-handed helix conformation induced by the optically active terminal group. Figure 1 also shows the temperature dependent circular dichroism (CD) spectra in isooctane of the polymers. Although no CD signal was observed around room temperature, as the temperature decreased below −20 °C, a bisignate CD signal was observed at $\lambda_{ext} = 340$ nm. The intensity of the CD signal increased with decreasing temperature. The appearance temperature of the CD band was almost parallel to the transition temperature in the UV absorption spectra. In the UV spectra, no significant differences are evident. This clearly indicates that the optically active terminal group induces the polysilane main chain to assume a preferential one-handed helical sense under this set of experimental conditions.

The bisignate induced CD effect is considered to be characteristic of exciton coupling between closely situated transition dipole moments on neighboring segments in the chiral supramolecule.[11] Thus, polysilanes generally consist of several segments with kinks, where the segment has different conformations with loose-helix at a kink. The optically active terminal group induces the segments of the polysilane main chain to assume a preferential one-handed helical sense, while the kinks would in turn the helical-sense of the segments.[4,12]

The helical-sense of the polymer can be controlled by the sign of the optically active terminal group. For example, the polymer with a (+)-menthoxy group at the polymer end showed a CD signal with a negative sign for the first Cotton effect at −40 °C. On the other hand, the polysilane with the optically active group having an opposite sign, i.e., the (−)-menthoxy group, showed a CD signal with a positive sign for the first Cotton effect at the same temperature (Fig. 2). The induced CD spectra were virtual mirror images of each other. The centers of these CD bands are the same as the absorption maxima of the polymers at the corresponding temperature. This means that the polysilanes adopt a helical conformation, but in opposite directions in the helical-sense as a result of different chiral stimuli from the (+)- or (−)-menthoxy group at the polymer end.[3,4] At present, the relationship between the sign of the Cotton effect in the CD spectrum and the screw-direction of the helix in the main chain is not clear. The comparison between the absorption and CD spectra also indicates that there is almost no population of the *anti* conformation, where the

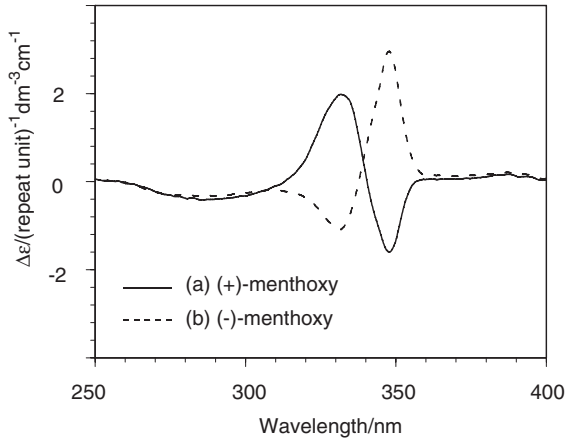

Fig. 2. CD spectra of polysilanes with: (a) a (+)-menthoxy ($M_n = 6800$), and (b) a (−)-menthoxy group ($M_n = 7200$) at the polymer end at −40 °C in isooctane.

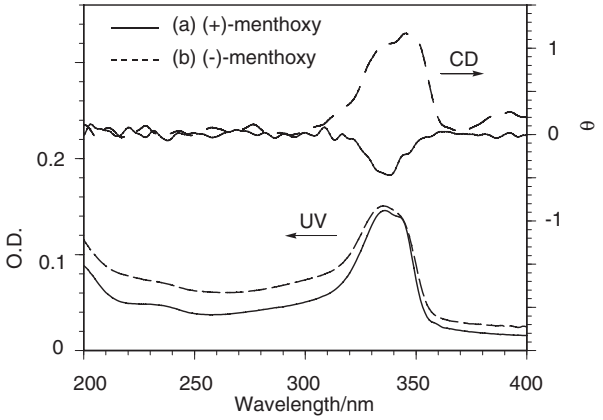

Fig. 3. UV and CD spectra of polysilanes with: (a) a (+)-menthoxy ($M_n = 6800$), and (b) a (−)-menthoxy group ($M_n = 7200$) at the polymer end in the solid state.

dihedral angle is 180°, which is expected to show absorption at longer wavelengths than the *transoid* conformation due to the more effective σ conjugation. Since the main chain assumes the predominant *transoid* conformation, where the dihedral angle is around 160–175°, as mentioned above, the helical pitch of the main chain may be around 15/7 helix.[13]

Dependence of Helical Induction on the Molecular Weight of the Polymers. The helical induction depends on the molecular weight of the polymer, because only the optically active terminal group of the polymer can induce the helical-sense, and so determine the screw-direction of the helix.[14,15] As listed in Table 1, the CD features were almost the same for the two types of polymers. However, the intensity decreased with increasing molecular weight, and approached the given value of the molar circular diachronic extremum ($\Delta\varepsilon_1$) for the polymers with a (+) and (−)-menthoxy group at the ends, respectively. It should be noted that in the screw-sense-polymerization of chiral monomers the $\Delta\varepsilon$ due to the helical induction of the polymer increases with increasing molecular weight and then reaches constant value,[15] where each monomer unit has a chiral side group that forms the stable single-handed structure predominantly. However, in our case, the polymer has only the optically active group at the polymer end. In the higher molecular weight polysilanes, helix reversals begin to occur and the induced helical conformation of the main chain breaks up as the molecular weight increases. This is consistent with the reported experimental results[15–18] and theoretical work.[19]

It seemed that the molecular weight dependence of the helical induction showed a different behavior in the polymer with (+) and (−)-menthoxy terminal groups. The $\Delta\varepsilon_1$ for the polymer with a (+)-menthoxy group decreased gradually with increasing molecular weight, but did not for the polymer with a (−)-menthoxy group at the polymer end. The optical activity for the polymer with a (−)-menthoxy group showed a slight increase at the second lowest molecular weight, as shown in Table 1. The origin of this strange behavior is more uncertain. A detailed description of the molecular weight dependence of the helical induction requires further studies. Okamoto and co-workers reported the chiroptical properties of oligomers of *m*-methylphenyl and alkyl isocyanate bearing an optically active end group.[17] In these studies, the gradual decrease of the specific rotation with increasing molecular weight was found, indicating the oligomer starts to undergo helix reversal until then the polymer chain, after a certain molecular weight, has equal amounts of right- and left-handed helical structures, which do not contribute to the optical activity.

Induction of Preferential One-Handed Helix Conformation in Polysilanes with an Optically Active Terminal Group in the Solid State. The helical induction was also observed in a film of the polymer with an optically active terminal group (Fig. 3). The sample for UV and CD measurements were prepared by coating a solution of the polymer in isooctane onto a quartz substrate followed by evaporation. The CD spectrum of the polymer with a (+)-menthoxy group at the polymer end in the solid state, even at room temperature, showed a negative Cotton signal at about 340 nm, where the polysilane chain takes a predominant *transoid* conformation, probably due to the restriction of the conformational mobility. In addition, the spectroscopic features are almost the same for the samples prepared by casting a solution of the polymer in a variety of concentrations. The CD spectrum of the polymer with a (−)-menthoxy group at the polymer end showed a Cotton signal, but the sign was positive. Again, the induced CD spectra were virtual mirror images of each other. This means that the polysilanes adopt a helical conformation, but in opposite directions in the helical-sense even in the solid state. In the solid state, the simple positive (or negative) CD signal can originate from intermolecular interactions.[20]

Preferential One-Handed Helix Conformation Induced by Aggregation of Polymers in a Good/Poor Mixed Solvent System. The helical induction was caused by aggregation of the polymer in a good/poor mixed solvent system. THF is a good solvent for the polysilanes, but MeOH is not. In THF, the polymer with the (−)-menthoxy group ($M_n = 2 \times 10^4$) showed an absorption maxima at 310 nm and did not show CD signals, because the polymer has a random-coil conformation. However, upon addition of MeOH to the THF solution of the polymer, a new absorption band appeared at around 340 nm in the UV spectra and an initial positive CD signal was observed at $\lambda_{ext} = 340$ nm. The intensity of the CD signal increased with increasing MeOH content, and the absorption

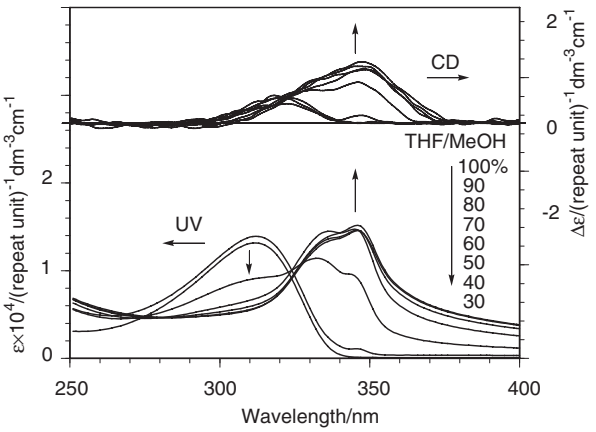

Fig. 4. UV and CD spectra of polysilanes with a (−)-menthoxy group at the polymer end ($M_n = 20000$) in a THF/MeOH mixed solvent system.

maxima shifted from $\lambda_{ext} = 310$ to 340 nm (Fig. 4). This indicates that the conformation of the polymer changed from a random-coil to the predominant *transoid* conformation with the formation of micro-aggregates during the addition of MeOH to the THF solution. Under these conditions, the polymer formed an optically active aggregate that synchronized the conformational changes of the polysilane main chain. Although such effects may originate from either intermolecular or intramolecular interactions, a filtration experiment proved that the size of the polymer aggregates was greater than 0.45 μm, showing that the interactions are largely intermolecular.[20] In the chiral aggregates, simple positive CD signals can originate from the intermolecular interaction, as observed in the solid state.

Summary

We have demonstrated the induction of a helical structure in polysilane with an optically active terminal group. Polysilanes with an optically active terminal (+) or (−)-menthoxy group, prepared by the anionic polymerization of masked disilene, adopted a preferential helical-sense conformation in solution at low temperatures and also in the solid state at room temperature. In this system, the terminal chiral information was encoded within the polymer, i.e., no chiral information could be detected at room temperature, but could be detected at low temperatures. The induction of the helical conformation of the polysilanes was also observed when forming aggregates in a good/poor mixed solvent system.

Experimental

Apparatus. 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, $\delta = 7.24$, ^{13}C, $\delta = 77.0$ for $CDCl_3$). The ^{29}Si chemical shift was referenced to external Me_4Si (0 ppm). GLC data was 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. UV spectra were recorded on a HP Agilent 8453 spectrometer. CD spectra were obtained on a JASCO J-820 spectrometer.

Chemicals. All starting materials were obtained from commercial suppliers and were used as received. (+) and (−)-Menthol were purchased from Tokyo Kasei (TCI, Tokyo). 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (cryptand 222) was purchased from Aldrich (Milwaukee, WI). Potassium was obtained from Nacalai Tesque (Kyoto). Benzene and toluene were dried over sodium/benzophenone and distilled under argon. These solvents were distilled again onto sodium under a high vacuum just before use. THF and methanol used for the spectroscopic measurements was of commercial UV spectral grade, and was used without further purification.

Synthesis of 1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene (Masked Disilene). 1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene was synthesized as described previously.[8] The reaction of 1,2-dichloro-1,1-dihexyl-2,2-dimethyldisilane with lithium biphenylide in THF at −78 °C gave the masked disilene in 62% yield. The monomer was purified by distillation and subsequently used for polymerization.

Anionic Polymerization of 1-Phenyl-7,7-dihexyl-8,8-dimethyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene. All the reactions were run under an atmosphere of argon. A typical example is as follows. The masked disilene (0.93 g, 2.26 mmol), cryptand 222 (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 (+)-menthoxide (0.114 mmol), prepared from the reaction of potassium and (+)-menthol in toluene, was added to the solution at room temperature. The mixture was stirred for 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 the polymer as a white powder (230 mg, 40%), with $M_n = 6.8 \times 10^3$, and $M_w/M_n = 1.3$, as determined by 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 34.3, 31.7, 22.8, 22.83, 14.1, 13.5, −0.66; ^{29}Si NMR ($CDCl_3$, 59 MHz) δ −27.5, −35.9; UV (isooctane, rt) $\lambda_{max} = 310$ nm; ($\varepsilon_{(Si–Si\ unit)} = 14500$).

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