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Helical Poly(alkylalkoxyphenylsilane)s Bearing Enantiopure Chiral Groups on the Phenyl Rings

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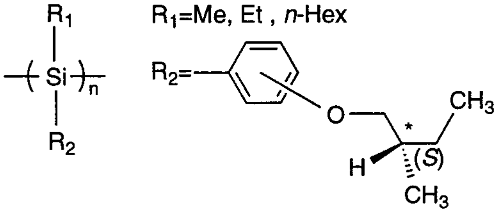
Synthesis and precise control of helical polymers are now vital subjects in basic and applied polymer chemistry[1−9] because of the technological importance of such materials, especially in the analysis and preparation of chiral drugs. A few synthetic helical polymers are known which can act as chiral selectors, tuned for a particular chiral drug and its mirror-image substance. For chiral selection, it is necessary to introduce some functional groups capable of discriminating between a pair of enantiomers through, for example, hydrogen bonding, phenyl $\pi-\pi$, dipole−dipole, ionic, or acid−base interactions. Recently, it has been demonstrated that, among synthetic helical polymers, optically active poly(dialkylsilane)s exhibit highly conformation-sensitive UV, fluorescence (FL), and circular dichroism (CD) bands due to the silicon σ-conjugating main chain.[9a−c,10] In addition, the helical conformational structures at a macroscopic or even microscopic level can be controlled by suitable choice of the alkyl side chain structures on the main chain.[9a−d] Helical poly(dialkylsilane)s, per se, however, do not reveal any chiral selection abilities due to the lack of functional selector groups. In this work, as a candidate for a chiral selector with multiple chiral recognition sites, we synthesized a series of new poly[alkyl-(*S*)-2-methylbutoxyphenylsilane] homopolymers **1**−**6**, with an enantiopure chiral group, a polar oxygen, and an aryl group, since there is no knowledge of the preparation and control of helical poly(alkylarylsilane)s bearing enantiopure chiral alkoxy groups on the phenyl rings so far. Herein we report the intriguing fact that the synthesis of poly(alkylarylsilane)s and the helical conformational structure are significantly affected by the position of the chiral alkoxy substituent on the phenyl ring, even though the chiral substituent is far from the main chain.

The desired substituted dichlorosilane monomers were prepared by condensation of the corresponding (*S*)-2-methylbutoxyphenyl Grignard reagents with the corresponding alkyltrichlorosilanes. The structures of the monomeric dichlorosilanes were supported by their analytical and spectral data. The results of monomer yields, boiling points, ^{29}Si and ^{13}C NMR, and the specific optical rotation are given in ref 12.

Scheme 1. Structures of Polysilanes 1−6



Polysilane	R1	R2
1	Me	*m*-position
2	Me	*p*-
3	Et	*p*-
4	*n*-Hex	*p*-
5 (low Mw)	Et	*m*-
6 (low Mw)	*n*-Hex	*m*-

Table 1. Synthesis and Optical Characterization[a] of Polysilanes 1−4

cmpd	yield[b]/ %	M_w[c] $\times 10^{-3}$	M_w/M_n	UV λ_{max}/ϵ^d	CD $\lambda_{max}/\Delta\epsilon^d$	FL−EM λ_{max}
1	13	850	4.4	325/8600	309/−0.59	352
2	7	40	3.2	351/7400		365
3	15	1400	2.6	352/7900		373
4	12	1500	2.5	359/17000		373

[a] UV and CD data recorded in tetrahydrofuran at 25 °C; FL data at 23−25 °C. [b] Isolated yields of high molecular weight fraction. [c] Molecular weights determined by gel permeation chromatography (GPC) and relative to polystyrene standards; eluant, tetrahydrofuran; 30 °C. [d] λ_{max} units, nm; ϵ and $\Delta\epsilon$ units, (Si repeat unit)$^{-1}$ dm^{-3} cm^{-1}.

Polymerization of the purified dichlorosilanes was performed according to the conventional Wurtz-type condensation.[13] The structures of polysilanes **1**−**4** are shown in Scheme 1. The yields, polymer properties, and the optical characterizations by UV, CD, and FL spectroscopies of **1**−**4** in tetrahydrofuran at 23−25 °C are summarized in Table 1. We also attempted to synthesize two other kinds of *m*-(*S*)-2-methylbutoxyphenyl substituted polysilanes with long alkyl chains by a similar method: poly[ethyl-*m*-(*S*)-2-methylbutoxyphenylsilane] (**5**) and poly[*n*-hexyl-*m*-(*S*)-2-methylbutoxyphenylsilane] (**6**). High molecular weight polymers were not obtained, however, presumably due to high steric hindrance.

The UV, CD, and FL spectra of **1** and **2** in tetrahydrofuran at 23−25 °C are shown in Figure 1, a and b, respectively. Interestingly, the profiles of the UV and CD spectra of **1** (Figure 1a) were somewhat unexpected. The most striking features in the UV spectrum of **1** are two absorptions at 290 and 325 nm, and in the CD spectrum, a marked negative peak at around 310 nm can be seen in the region between the two UV bands. The presence of a band in the CD spectrum indicates that **1**, bearing a chiral group in the meta position on the phenyl ring, adopts a prevailing screw-sense helical backbone. In the UV spectrum of **1**, the long-wavelength absorption at around 325 nm may be assigned to the lowest Si $\sigma-\sigma^*$ interband transition. However, this absorption occurs at shorter wavelength than that for poly(methylphenylsilane) (PMPS) (ca. 341 nm) in solution.[10a] This UV blue shift is likely to be due to steric imbalance between the methyl and bulky *m*-(*S*)-2-methylbutoxyphenyl side pendants which may be greater in this case than for PMPS. The helical backbone of **1**, therefore, may be strongly distorted, twisted, and folded. On the other hand, the assignment of the absorption at around 290 nm is not clear. Two possible origins can, however, be considered as follows: (1) This peak originates in a different screw pitch of the helical backbone; i.e., **1** contains two types of helical pitches, one loose and one tight. This hypothesis is supported by the presence of a negative Cotton band extending over the two UV bands. (2) This peak is based on the absorption

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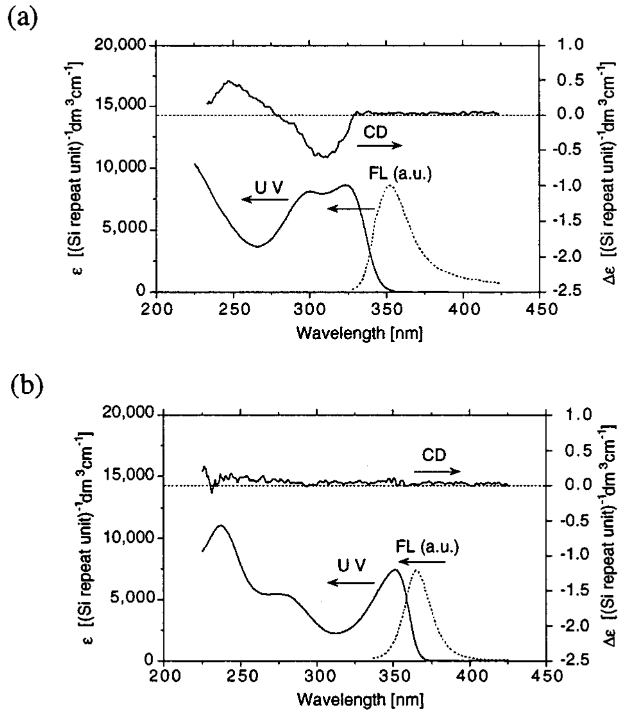

Figure 1. UV, CD, and FL spectra of (a) poly[methyl-*m*-(*S*)-2-methylbutoxyphenylsilane], **1**, and (b) poly[methyl-*p*-(*S*)-2-methylbutoxyphenylsilane], **2**, in tetrahydrofuran at 23−25 °C.

due to the phenyl $\pi-\pi^*$ transition affected by the σ orbitals of the Si main chain. The bulky *m*-(*S*)-2-methylbutoxyphenyl chiral side pendants may be positioned in an offset, stacked face-to-face arrangement, perpendicular to the main-chain axis to diminish steric hindrance. As a result, $\sigma-\pi$ orbital mixing may occur, and the UV peak associated with the $\pi-\pi^*$ transition is shifted to slightly longer wavelength compared with that of PMPS (observed at around 280 nm).

The UV and CD spectra of **2** (Figure 1b) with a chiral group in the para position are considerably different from those of **1**. The UV $\lambda_{\max}$ of **2** was shifted about 10 nm to longer wavelength than that of **1**, indicating that the energy of the $\sigma-\sigma^*$ transition of the Si main chain appears to depend on the position of the electron-donating chiral alkoxy moiety, meta or para, on the phenyl ring. Electron donation from the para chiral alkoxy moiety may contribute more effectively to the σ-conjugating Si main chain through the phenyl ring. This is because it is possible to consider resonance hybrid structures of a para derivative, one of which causes an increase of electron density at the σ-conjugated Si backbone, and would be expected to have a significant substituent effect on the UV properties.

In the CD spectrum of **2**, no bands were observed even at −80 °C. This is because although **2** is considered to be helical, the Cotton band of para derivatives would be canceled by oppositely signed CD bands originating in opposite screw-sense helical structures. It is thus apparent that the helical backbone conformation is controlled by the position of the chiral substituent on the phenyl ring. The Si main chain of meta derivatives such as **1** adopts a preferential helical screw sense due to chiral steric effects, while this effect is much smaller in para derivatives such as **2** and does not affect the Si main-chain conformation. The difference of the helical conformations between meta and para derivatives may be due to conformational locking (and the degree of steric hindrance to (*S*)-2-methylbutoxy-substituted phenyl ring rotation). Since para derivatives may have enough space to rotate the *p*-(*S*)-2-methylbutoxyphenyl group freely, backbones in these systems are not conformationally locked. Therefore, although the backbone of **2** is helical, there is no dominant screw-sense selectivity. Consequently, it is clear that the optical properties and the induction of a preferential helical screw sense can be controlled by the chiral center position, even though it is far from the Si backbone.

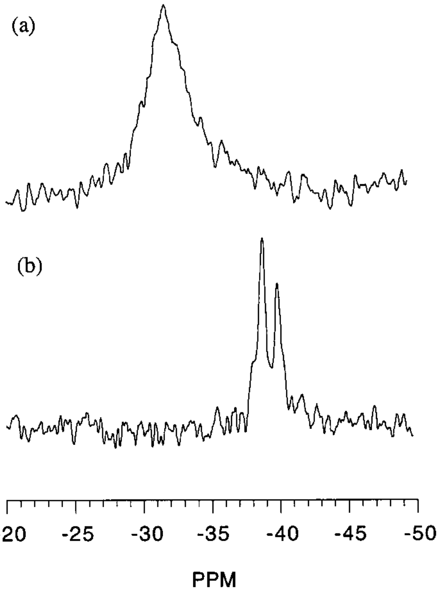

Figure 2. ^{29}Si NMR spectra of (a) poly[methyl-*m*-(*S*)-2-methylbutoxyphenylsilane], **1**, and (b) poly[methyl-*p*-(*S*)-2-methylbutoxyphenylsilane], **2**, in benzene-d_6 at 50 °C. Spectra are referenced externally to TMS.

The CD spectra of **3** and **4**, which have longer alkyl chains than **2**, show similar features to that of **2**. No Cotton band was observed at temperatures down to −80 °C. These results also are important evidence that the induction of a preferential helical screw sense depends on the position of the chiral group on the phenyl ring.

To investigate the difference between Si main-chain structure in **1** and **2** in detail, we measured the ^{29}Si NMR spectra in benzene-d_6 at 50 °C (shown in Figure 2). In these spectra, a broad signal (around −32 ppm, $\Delta\nu_{1/2}$ about 240 Hz) was observed in **1**, and two sharp signals (about −39 and −40 ppm, $\Delta\nu_{1/2}$ about 76 and 85 Hz, respectively) and one shoulder (about −38 ppm) were observed in **2**. The two sharp signals of **2** may reflect the tacticity[14] of the Si main chain, with syndiotactic triads at −39 ppm and isotactic triads at −40 ppm. (The shoulder at −38 ppm may be assigned to heterotactic triads.) The broadness of the signal of **1** suggests that the mobility of the Si main chain of **1** is considerably restrained, presumably because the chiral steric effect locks the Si main-chain conformation in a predominant helical screw sense. In contrast to **1**, the Si main chain of **2**, which shows sharp peaks, is in fast motion; thus, *P* (plus) and *M* (minus) helical segments can exchange easily without locking into a partial screw sense. This must be the reason for optical inactivity of **2** in tetrahydrofuran solution.

In summary, we have described the first examples of poly(alkylarylsilane) homopolymers whose optical properties and helical conformations are controlled by the position of the chiral group, i.e., remote-controlled polysilanes. It is found that the meta derivative is optically active in solution, while para derivatives are optically inactive despite bearing enantiopure chiral groups, since para derivatives contain equivalent *P* and *M* helical segments. If the main-chain conformations of para derivatives are locked into one screw sense only, either *P* or *M* helical segments, by some external stimulus (e.g., chiral molecule or achiral solvents), the “masked helicity” of the para derivatives may appear in solution. The next challenging subject is to confirm the chiral recognition phenomenon between optically active polysilanes **1**−**4** and enantiomers, aiming at chiral stationary phases for high-performance liquid chromatograpy. This work is now in progress.

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(12) (a) The desired substituted dichlorosilane monomers were prepared by the condensation of the corresponding (*S*)-2-methylbutoxy-substituted phenyl Grignard reagent with the corresponding alkyltrichlorosilanes. The monomer data[12b] are as follows. Methyl-*m*-(*S*)-2-methylbutoxyphenyldichlorosilane: yield, 64.6%; bp, 110−115 °C/0.8 mmHg. ^{29}Si NMR: 18.20 ppm. ^{13}C NMR: 7.04, 11.25, 16.79, 26.11, 34.73, 73.10, 110.65, 120.60, 133.73, 135.75, 163.50 ppm. $[\alpha]^{22}_{D} = +6.23°$ (neat). Methyl-*p*-(*S*)-2-methylbutoxyphenyldichlorosilane: yield, 47.2%; bp, 122−125 °C/1.0 mmHg. ^{29}Si NMR: 18.64 ppm. ^{13}C NMR: 5.71, 11.28, 16.49, 26.11, 34.65, 72.77, 114.61, 124.15, 134.82, 162.15 ppm. $[\alpha]^{24}_{D} = +7.51°$ (neat). Ethyl-*p*-(*S*)-2-methylbutoxyphenyldichlorosilane: yield, 56.1%; bp, 102−105 °C/0.15 mmHg. ^{29}Si NMR: 20.57 ppm. ^{13}C NMR: 6.31, 11.29, 13.31, 16.51, 26.14, 34.68, 72.79, 114.63, 123.09, 135.17, 162.15 ppm. $[\alpha]^{23}_{D} = +7.26°$ (neat). *n*-Hexyl-*p*-(*S*)-2-methylbutoxyphenyldichlorosilane: yield, 49.0%; bp, 140−145 °C/0.35 mmHg. ^{29}Si NMR: 19.28 ppm. ^{13}C NMR: 11.30, 14.05, 16.51, 20.01, 22.49, 22.54, 26.15, 31.33, 32.11, 34.69, 72.79, 114.61, 123.47, 135.14, 162.10 ppm. $[\alpha]^{22}_{D} = +6.09°$ (neat). (b) ^{29}Si NMR (59.59 MHz) and ^{13}C NMR (75.43 MHz) were recorded in $CDCl_3$ solution referenced to external TMS.

(13) The polymerization of the purified dichlorosilanes was performed according to the conventional Wurtz-type condensation as follows. The synthesis of **1** is representative. To a mixture of 16 mL of dry toluene, 1.3 g (0.06 mol) of sodium dispersion, and surface-activated by diglyme (10 μL), 4.0 g (0.014 mol) of methyl-*m*-(*S*)-2-methylbutoxyphenyldichlorosilane was added dropwise in an argon atmosphere. The mixture was stirred slowly at 110 °C, monitoring the molecular weight periodically. After 2 h, 0.1 equiv of trimethylchlorosilane was added as terminator, and stirring continued for a further 30 min and then cooled to room temperature. The mixture was hydrolyzed with ethanol and water. The organic layer was separated and washed with water. After the solvent was removed, the remaining crude polymer was reprecipitated from toluene−ethanol solution. The high molecular weight fraction was obtained as a white powder, separated by centrifugation, and vacuum-dried in an oven at 90 °C for 5 h. The yields and some properties of polysilanes **1**−**4** obtained in this work are summarized in Table 1.

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