Precise Control of Optical Properties and Global Conformations by Marked Substituent Effects in Poly(alkyl(methoxyphenyl)silane) Homo- and Copolymers

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ABSTRACT: A series of poly(alkyl(methoxyphenyl)silane) homopolymers and poly[(alkyl(methoxyphenyl)-silane)-*co*-((*S*)-2-methylbutyl(methoxyphenyl)silane)] copolymers containing 20% chiral monomer units were synthesized, and marked substituent effects on their absorption characteristics and the global and local conformations in THF solution were observed. In the homopolymers, upon increase of the alkyl side chain length, the global backbone conformations changed from a considerably shrunken random coil to a stiff extended structure, and the UV absorptivity and absorption wavelength maximum in the Si main chain region were easily controlled by a combination of the alkyl substituents and position of the methoxy group on the phenyl ring. In the achiral−chiral copolymers, preferential screw-sense helical conformations of the Si backbone were induced by the cooperative effect of the chiral substituents. In addition, we found that the sign of the circular dichroism (CD) peak in the aryl absorption region of the copolymers depended on the methoxy group position in chiral monomer units.

Introduction

Recently, intensive studies on synthetic polymers that show unique electrical and (chir)optical properties have been performed with a view to developing future functional materials. Polysilanes are an exciting class of semiconducting and chromophoric polymers, consisting of a linear chain of Si atoms, and the occurrence of conjugated σ-bonding in the Si backbone is responsible for a variety of interesting electrical and (chir)optical properties.[1−4] For instance, photoconduction and hole conduction,[5] the enhancement of electrical conductivity by doping,[6] electroluminescence (EL),[7] third-order nonlinear effects,[8] and various chromism phenomena in response to external stimuli (thermo-, piezo-, solvato-, and surface-mediated chromism)[9] have been reported. In addition, several practical developments for polysilanes such as in microlithography, as precursors to silicon carbide, and in EL devices have been established, and the polymers have also recently been considered as a candidate for a molecular wire.[10] Polysilane research has therefore seen intense activity as new materials are sought for future device applications. These soluble polysilanes may also be viable from a commercial point of view because of the relative ease of material processing (large area thin films, etc.), low cost, and chemical tunability of the optoelectronic properties through choice of the two organic side chains.

It is also well-known that the conformational structures of the Si backbone at a macroscopic or even microscopic level can be controlled by a suitable choice of the side chain structures, and consequently, its optoelectric properties (related to the band gap) are tailored by adjustment of the band positions through substituent effects.[1,2,11−13] Especially, in phenyl-substituted polysilanes, an electronic interaction between the delocalized Si chain σ-bonding orbitals and some of the π orbitals located on the aryl rings occurs, and a dramatic modification and precise control of both the band gap and conformational structure have been demonstrated for the optical properties in the Si backbone region.[2,11f−h,12,13] Additionally, we have demonstrated that an enantiopure chirally substituted poly(dialkyl- or diarylsilane)s may adopt a preferential helical screw-sense Si backbone and exhibit a thermodriven circular dichroism (CD) switching effect based on a *right*−*left* helical transition in the solution state.[11a,12b] These polysilanes may be potential candidates for application in a molecular-based chiroptical switch and memory in the UV/vis region. In addition, in poly(alkyl(alkoxyphenyl)silane)s bearing a remote chiral group on the phenyl ring, the optical properties and helical conformations may be controlled by the position of the chiral group, *m*- or *p*-position,[13a] and in the aggregated state, the polysilanes showed unique, switchable CD properties due to higher-order chiral structural changes, controllable by the solvent polarity or sample temperature.[13b] The poly(alkyl(alkoxyphenyl)-silane)s have also exhibited chirality recognition ability for two mirror-image guest enantiomers (chiral alcohols). Since these polysilanes have polar oxygen groups and aryl groups on the backbone, they are capable of multiple and weak interactions between the guest enantiomers and host polymer through hydrogen-bonding and/or phenyl $\pi-\pi$ interactions.[13c] Therefore, this polysilane may open the intriguing possibility to assist in the design of a new polymer-based chiral stationary phase in gas or liquid chromatography or chiral sensors.

The present paper describes the synthesis and precise control of the optical properties and both global and local conformations of poly(alkyl(alkoxyphenyl)silane)s. Polymers with a variety of substituents were made, so as to both identify the photochemistry systematically and provide insight into these unique, functional materials, the properties of which depend on the slight difference in side pendant structures. In the poly(alkyl(methoxyphenyl)silane) homopolymers in dilute solution, upon increase of the alkyl side chain length, the global conformations could be controlled from a considerably shrunken random coil to a stiff extended structure, and the UV absorption properties could be also controlled

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due to substituent effects resulting from the difference of methoxy group position on the phenyl ring as well as the alkyl chain length. In the polysilane copolymers incorporating chiral monomer units, single screw-sense helical conformations were induced by the cooperative effect of the chiral substituents which exhibited unique chiroptical properties in the phenyl region due to the phenyl pendant arrangements.

Experimental Section

Analysis. UV and CD absorption spectra were recorded simultaneously on a JASCO J-720 spectrometer equipped with a Peltier controller for temperatures at 20 °C (1 cm path length quartz cell, concentration ca. 1×10^{-4} or 5×10^{-5} mol/L). Fluorescence (FL) and FL anisotropy (FL-A) spectra were measured using a Hitachi F-850 spectrofluorometer at room temperature. NMR spectra were recorded on a Varian Unity 300 NMR spectrometer relative to internal TMS in $CDCl_3$ for silicon at 59.59 MHz and for carbon at 75.43 MHz. The weight-average molecular weight (M_w), number-average molecular weight (M_n), polydispersity, and in-line absorption spectra of the polysilanes were determined by size exclusion chromatography (SEC) on a Shodex mixed gel KF80M column with THF as eluent at 30 °C (Shimadzu A10 series HPLC apparatus equipped with a diode array detector, deaeration unit, and double-plunger pump), based on a calibration with polystyrene standards. Optical rotation at the Na D line was measured in the neat state at room temperature with a JASCO DIP-370 polarimeter using a quartz cell with a path length of 10 mm.

Viscometric Studies. Viscometric measurements of polysilanes **1**−**6** were performed by the Toray Research Center (Shiga, Japan) using an in-line configuration of viscometer (Viscotek H502a, equipped with a capillary of dimensions 0.5 mm i.d. × 61 cm length) and SEC (Waters 150C). Concerning the viscometric measurements of polysilanes **7**−**11**, these were performed using an in-line configuration of a viscometer (Viscotek T60A) and SEC (Shimadzu) instrument. The solvent was THF, and the measurement temperature was 30 °C. Molecular weights were determined from a universal calibration plot, and the corresponding intrinsic viscosities, $[\eta]$, were obtained from the viscometer. Application of the Mark−Houwink−Sakurada equation (eq 1) in a plot of log$[\eta]$ vs log molecular weight, M, affords the viscosity index, α, and constant, K, from the slope and intercept, respectively.

$$[\eta] = KM^{\alpha} \tag{1}$$

The radius of gyration, R_g, at a given molecular weight, M, may be derived from eq 2, where Φ is the Flory constant (2.86×10^{-23} mol^{-1}).

$$[\eta]M = \Phi(6R_g^{\,2})^{3/2} \tag{2}$$

Monomer Synthesis. All of the apparatus was oven-dried, and standard techniques were employed for handling air- and moisture-sensitive compounds. Solvents and alcohols were purchased dry and stored over type 4A molecular sieves. The desired substituted dichlorosilane monomers were prepared by the condensation of the corresponding methoxyphenyl Grignard reagent with the corresponding alkyltrichlorosilanes. The monomer data are as follows. Methyl-*m*-methoxyphenyldichlorosilane: yield, 50.5%; bp, 87−90 °C/3.50 mmHg. ^{29}Si NMR: 18.54 ppm. ^{13}C NMR: 5.50, 55.25, 117.28, 118.25, 125.16, 129.71, 134.73, 159.32 ppm. Methyl-*p*-methoxyphenyldichlorosilane: yield, 49.7%; bp, 85−88 °C/1.20 mmHg. ^{29}Si NMR: 18.70 ppm. ^{13}C NMR: 5.70, 55.19, 114.06, 124.51, 134.89, 162.33 ppm. Ethyl-*m*-methoxyphenyldichlorosilane: yield, 66.6%; bp, 80−85 °C/0.70 mmHg. ^{29}Si NMR: 20.39 ppm. ^{13}C NMR: 6.25, 13.05, 55.25, 117.25, 118.61, 125.55, 129.62, 133.78, 159.32 ppm. Ethyl-*p*-methoxyphenyldichlorosilane: yield, 78.1%; bp, 85−88 °C/0.60 mmHg. ^{29}Si NMR: 20.64 ppm. ^{13}C NMR: 6.283, 13.227, 55.173, 114.051, 123.399, 135.210, 162.299 ppm. *n*-Hexyl-*m*-methoxyphenyldichlorosilane: yield, 71.4%; bp, 123−126 °C/0.80 mmHg. ^{29}Si NMR: 19.04 ppm. ^{13}C NMR: 14.03, 20.66, 22.40, 31.26, 32.06, 55.22, 117.16, 118.54, 125.48, 129.64, 134.10, 159.27 ppm. *n*-Hexyl-*p*-methoxyphenyldichlorosilane: yield, 72.3%; bp, 122−125 °C/0.50 mmHg. ^{29}Si NMR: 19.34 ppm. ^{13}C NMR: 14.04, 20.90, 22.46, 31.28, 32.07, 55.18, 114.01, 123.75, 135.15, 162.23 ppm. (*S*)-2-Methylbutyl-*m*-methoxyphenyldichlorosilane: yield, 34.2%; bp, 80−85 °C/0.18 mmHg. ^{29}Si NMR: 18.78 ppm. ^{13}C NMR: 11.15, 21.80, 28.36, 30.32, 32.31, 55.28, 117.09, 118.58, 125.52, 129.63, 134.75, 159.26 ppm. $[\alpha]^{22}_{D} = +6.23°$ (neat). (*S*)-2-Methylbutyl-*p*-methoxyphenyldichlorosilane: yield, 41.3%; bp, 84−87 °C/0.10 mmHg. ^{29}Si NMR: 19.07 ppm. ^{13}C NMR: 11.16, 21.79, 28.61, 30.37, 32.31, 55.10, 114.02, 124.33, 135.14, 162.21 ppm. $[\alpha]^{22}_{D} = +14.99°$ (neat).

Polymer Synthesis. Polymerization of purified dichlorosilanes was performed according to the conventional Wurtz-type condensation as follows. The synthesis of **1** is representative. To a mixture of 25 mL of dry toluene was added 2.1 g (9.1×10^{-2} mol) of sodium surface-activated by diglyme (10 μL) and 5.0 g (2.0×10^{-2} mol) of methyl-*m*-methoxyphenyldichlorosilane dropwise under an argon atmosphere. The mixture was stirred slowly at 110 °C, while 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, after which the mixture was pressure filtered through two Teflon membranes (pore size 40 and 10 μm). The high molecular weight fraction ($M_w = 19\,000$, yield 19%) was isolated by centrifugation after fractional precipitation in a mixed 2-propanol−toluene solution and vacuum-dried at 90 °C overnight. Concerning the synthesis of copolymer **7**, methyl-*m*-methoxyphenyldichlorosilane (6.4 g, 2.9×10^{-2} mol) and (*S*)-2-methylbutyl-*m*-methoxyphenyldichlorosilane (2.0 g, 7.2×10^{-3} mol) were combined to give a mixture in the ratio 4:1 and added in toluene to 4.0 equiv of sodium in toluene at 110 °C. The yields and some properties of polysilanes **1**−**11** obtained in this work are summarized in Table 1. Even though it is difficult to obtain reliable integration data from the NMR spectra of the polymers due to the presence of broad and, in some cases, overlapping peaks, we confirmed that the copolymers contain achiral and chiral units in an almost 4:1 ratio from the NMR relative intensities. We also attempted to synthesize poly[(methyl(*m*-methoxyphenyl)silane)$_{0.8}$-*co*-((*S*)-2-methylbutyl(*p*-methoxyphenyl)silane)$_{0.2}$] (**12**), poly[(*n*-hexyl(*m*-methoxyphenyl)silane)$_{0.8}$-*co*-((*S*)-2-methylbutyl(*m*-methoxyphenyl)silane)$_{0.2}$] (**13**), and poly[(*n*-hexyl(*m*-methoxyphenyl)silane)$_{0.8}$-*co*-((*S*)-2-methylbutyl(*p*-methoxyphenyl)silane)$_{0.2}$] (**14**) by a similar method. High molecular weight polymers were not obtained, however, presumably due to high steric hindrance.

Results and Discussion

Optical Spectroscopy and Global Conformations of Polysilane Homopolymers 1−6. The UV spectra of polysilanes **1**−**6** in THF at 20 °C are shown in Figure 1, and their UV characteristics are summarized in Table 1. Figure 1 exhibits optical properties typical of poly(alkylarylsilane)s. Polysilanes **1**−**6** show a strong absorption peak associated with a delocalized, lowest Si $\sigma-\sigma^*$ interband transition, which might be also affected by the phenyl ring ($\pi \rightarrow \sigma^*$ mixing; charge transfer, ring to chain).[2,14] The weak, broad absorption at around 270 nm is assigned to the phenyl $\pi-\pi^*$ transition, though the *m*-methoxy-substituted **1**, **3**, and **5** show split absorption bands in this region, which might be due to the asymmetric vibration of electron-donating methoxy groups on the phenyl ring. The UV absorption properties of **1**−**6** in the Si backbone region are dramatically dependent on the alkyl side chain length (UV λ_{max} shifts from 338 to 358 nm with considerable increase of UV absorptivity (ϵ/Si repeating units) and decrease of full width at half-maximum (fwhm) value with increase of the alkyl chain length). The great difference in the

Table 1. Synthesis and Optical Characterization[a] of Polysilane Homo- and Copolymers 1−11

cmpd	yield[b]/%	M_w[c] × 10^{-3}	M_w/M_n[d]	UV[e] λ_{max}/ϵ/fwhm	CD[e] $\lambda_{max}/\Delta\epsilon$	FL-EM λ_{max}	FL-A[f]	α
1	19	19	2.0	339/6400/32.5		353	−0.02−0.31	0.45
2	10	23	3.7	348/4300/37.4		366	0.04−0.27	0.35
3	1.7	1300	3.0	338/11000/33.3		360	0.01−0.23	0.63
4	6.5	770	3.3	351/7600/34.4		374	0.02−0.22	0.64
5	1.0	320	4.1	348/18000/15.7		358	0.02−0.17	0.96
6	6.8	250	3.4	358/14000/19.1		371	0.04−0.17	0.94
7	0.60	450	2.1	339/7700/34.2	342/0.71 282/0.22	356	0.01−0.29	0.76
8	4.4	780	2.1	350/7400/31.0	353/0.70 284/0.18	366	−0.07−0.18	0.65
9	2.7	820	2.2	352/8500/31.3	354/0.93 286/−0.57	367	0.02−0.24	0.70
10	1.8	750	3.4	360/9400/18.7	360/0.76 284/0.14	373	0.02−0.23	0.98
11	5.7	590	3.3	363/12000/20.1	362/1.26 288/−0.79	375	0.02−0.22	0.90

[a] UV and CD data recorded in THF at 20 °C; fluorescence (FL) and fluorescence anisotropy (FL-A) data in THF at room temperature (23−25 °C). [b] Isolated yields of high molecular weight fraction. [c] Molecular weights determined by size exclusion chromatography (SEC) and relative to polystyrene standards; eluant: THF; 30 °C. [d] Polydispersity index: M_w/M_n; given for isolated high M_w fractions. [e] λ_{max} units: nm; ϵ and $\Delta\epsilon$ units: (Si repeat unit)$^{-1}$ dm^{-3}cm^{-1}; fwhm = full width (nm) and half-maximum of λ_{max}. [f] FL-A measured over region of backbone σ−σ^* transition.

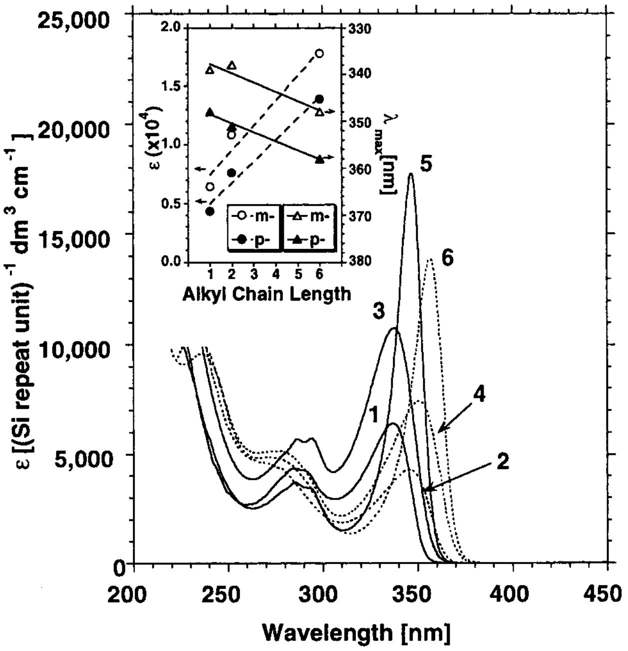


Figure 1. UV spectra of poly(alkyl(methoxyphenyl)silane)s **1**−**6** in dilute THF solution at 20 °C. Inset: plot of UV λ_{max} and molar absorptivities (ϵ) per Si repeat unit vs alkyl side chain length for **1**−**6**.

absorption properties of **1**−**6** is considered to be essentially associated with the differences of the polymer global conformation. Such correlations between the global conformations of polysilanes and their UV absorption characteristics have been experimentally established for over 20 types of poly(dialkylsilane)s, poly(alkylphenylsilane)s, and poly(diarylsilane)s bearing linear and/or branched alkyl substituents.[11b,12c] On the basis of the systematic results from the UV data, viscosity index, α, and ^{29}Si NMR line width, the polysilanes have been classified as able to adopt shrink coil, flexible coil, stiff, and rigid-rod-like conformations. We also investigated the correlation between α and ϵ in poly(alkyl(methoxyphenyl)silane)s **1**−**6** (Table 1), with the result that the global conformations of methyl-substituted (**1**, **2**), ethyl-substituted (**3**, **4**), and *n*-hexyl-substituted (**5**, **6**) polysilanes appear to correspond to a considerably shrunken random coil, a flexible coil, and a stiff extended structure, respectively. This substituent size dependence apparently is due to steric interference between pendant groups either 1,2 or 1,3 to each other, which can result in Si−Si bond lengthening and/or a change in the equilibrium content of the trans and gauche conformations. In addition, the UV absorption spectra of **1**−**6** also show a marked substituent effect in the local backbone conformations, dependent on the position of the electron-donating methoxy group on the phenyl ring. The UV λ_{max} of *p*-substituted derivatives (**2**, **4**, and **6**) are shifted about 10 nm to longer wavelength than that of the corresponding *m*-substituted derivatives (**1**, **3**, and **5**), indicating that the electron donation from the *p*-alkoxy moiety may contribute more effectively than the *m*-alkoxy moiety to the σ-conjugating Si main chain through the phenyl ring. This is because it is possible to consider resonance hybrid structures of the *p*-derivatives, 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.[13a] The lower ϵ values of *p*-derivatives compared to the corresponding *m*-derivatives might also imply greater local conformational randomness in the Si backbone of the *p*-derivatives.

Parts a, b, and c of Figure 2 illustrate the UV absorption, fluorescence (FL), and FL anisotropy (FL-A) data for **1**, **2**, and **5** in THF at room temperature (23−25 °C), respectively. For **1** and **2** (methyl derivatives), FL emission occurs at 353 and 366 nm, giving a Stokes shift of about 14 and 18 nm, respectively. The FL emission profiles with fwhm ≈ 20 nm in both cases are not mirror images of the corresponding UV absorption spectra, and the FL-A around the Si σ−σ^* interband region exhibits a strong dependence on photoexcitation wavelength (Table 1). In contrast, for **5** (*n*-hexyl derivative), FL emission occurs at 358 nm (10 nm Stokes shift) and has a completely mirror-image profile to the UV spectra, and the FL-A is only weakly dependent on the photoexcitation wavelength over the region of the Si main-chain absorption. These results, importantly, indicate also that the polysilane conformational structures and photophysical properties in solution are greatly influenced by the substituent structures.[11h] The absorp-

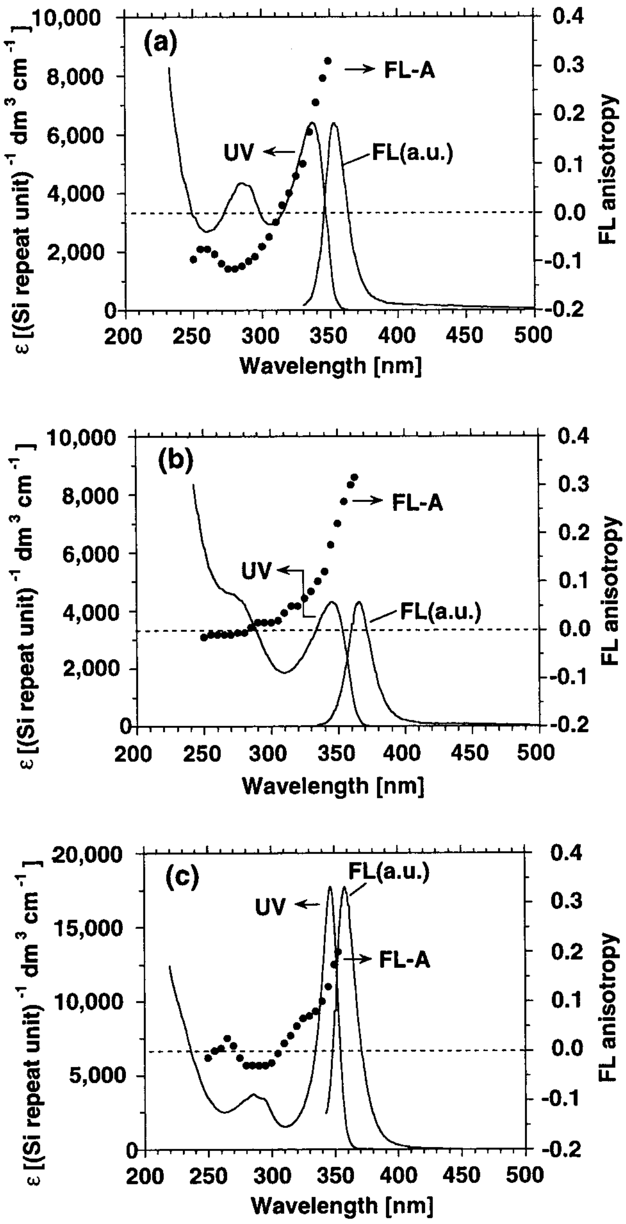


Figure 2. UV, FL excited at UV $\lambda_{\max}$, and FL-A spectra of (a) **1**, (b) **2**, and (c) **5** in dilute THF solution at room temperature (20–23 °C).

tion spectra of polysilanes originate from a composition of various segmented chromophores with different excitation energies. However, emission occurs from the segmented chromophores with the lowest excitation energies, since photoexcited electron–hole pairs in segments with higher energy absorption transfer into the lowest excitation energy level. The mirror-image profiles of the narrow UV absorption and emission in **5** therefore show that the backbone conformation has a more regular spatial conformation with relatively fewer twists or kinks. This may be consistent with the result that **1** and **2** adopt a random-coil and **5** has a stiff global conformational structure in solution.

Interestingly, the FL-A values of all *m*-derivatives (**1**, **3**, and **5**) in the phenyl absorption region (270–290 nm) are negative (excitation wavelength; UV $\lambda_{\max}$ of Si σ–σ^* interband transition). Theoretically, the FL-A value is defined from -0.2 ($\omega = 90°$) to 0.4 ($\omega = 0°$), where ω is the angle between the absorption moment, *A*, and emission moment, *E*.[15] The negative FL-A values in the *m*-derivatives may therefore imply a relatively close to orthogonal arrangement between the sterically hindered, *m*-methoxyphenyl groups and the Si main chain, though the detailed structures are not yet clear.

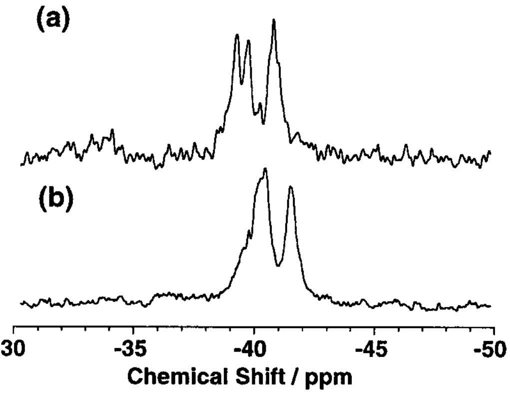


Figure 3. ^{29}Si NMR spectra of (a) **1** and (b) **2** in chloroform-d_3 at 30 °C. Spectra are referenced externally to TMS.

It has been suggested that introduction of undesired structural defects, i.e., Si–Si–Si branching defects caused by photodecomposition of the polymer and insertion of the resulting silylene radical into the backbone, could markedly affect the photophysical properties (FL excitation and emission characteristics) of polysilanes.[2b,16] Polysilanes **1**–**6**, however, exhibit typical narrow excitation and emission spectra in the UV region, and no additional broad red-shifted band is detectable in the room-temperature solution FL emission spectra. This indicates that **1**–**6** appear to have a very low level of Si backbone defects and that no branching has occurred.

Investigations of Local Structures of Polysilanes 1 and 2 by ^{29}Si NMR Measurements. To investigate the Si main-chain local structure, we measured the ^{29}Si NMR spectra of **1** and **2** in CDCl$_3$ at 30 °C (shown in Figure 3). In the spectrum of **1**, several significant signals (ranging from -42 to -38 ppm) are clearly observed, which may reflect the tacticity of the Si main chain. (The possible local configurations of the Si main chain are considered to be syndiotactic, isotactic, and heterotactic triads.[3d,13a]) In contrast, the ^{29}Si NMR spectrum of **2** with *p*-methoxy groups on the phenyl ring shows only two broad signals at around -41.5 and -40.4 ppm, though the downfield signal seems to have a shoulder at around -40 ppm. (The signals may be due to the overlap of intricate higher ordered tacticity.) The broad signals in **2** may result from the randomness of the Si main-chain conformations, as is consistent with the lower ϵ value in the UV spectra compared to **1**. In addition, all signals in **2** are shifted by about 0.5 ppm upfield compared with that of **1**. This result indicates that electron donation from the *p*-alkoxy moiety could occur more effectively and increase the electron density in the Si main chain. (^{13}C NMR spectra in the methyl and phenyl region of both **1** and **2** in CDCl$_3$ at 30 °C are shown in the Supporting Information.) The NMR data thus also indicate a marked substituent effect depending on the position of the methoxy groups which may affect the local environment of poly(alkyl(alkoxyphenyl)silane)s.

Cooperative Helical Order Effects and Unique Chiroptical Properties in Optically Active Poly(alkyl(alkoxyphenyl)silane) Copolymers. To investigate cooperative helical backbone ordering, we prepared poly(alkyl(alkoxyphenyl)silane) copolymers **7**–**11**,

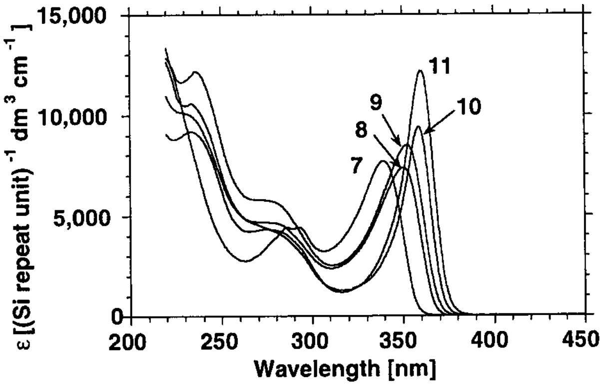


Figure 4. UV spectra of poly(alkyl(methoxyphenyl)silane) copolymers containing 20% chiral monomer units, **7**–**11**, in dilute THF solution at 20 °C.

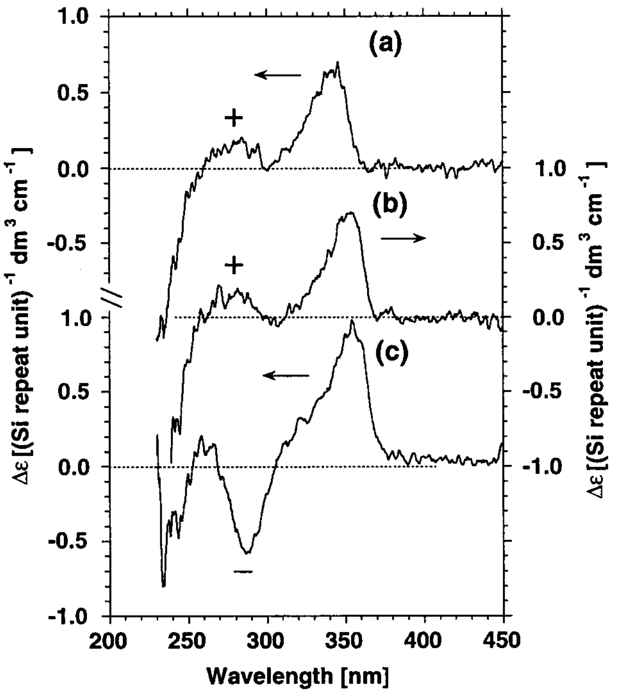
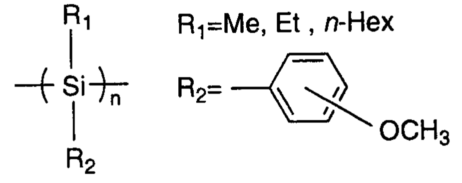


Figure 5. CD spectra of (a) **7**, (b) **8**, and (c) **9** in dilute THF solution at 20 °C.

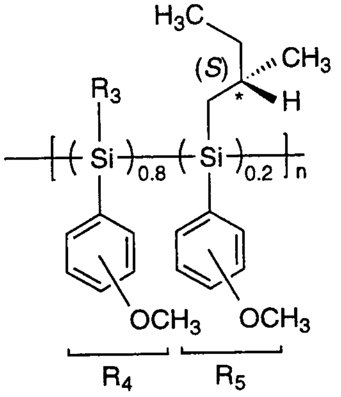
containing 20% (*S*)-2-methylbutyl-substituted methoxyphenylsilane monomer units. The UV and CD spectra of achiral–chiral copolymers **7**–**11** are shown in Figures 4–6. In the UV spectra of **7**–**11** (Figure 4), the UV λ_{max} are slightly red-shifted compared with the corresponding achiral homopolymers **1**–**6**, indicating that the Si main-chain backbone may be more extended due to steric effects caused by the introduction of the branched chiral groups. Additionally, for copolymers **8**–**11** (R_4; *p*-position, Scheme 1), when R_5 in the chiral monomer unit is *p*-methoxyphenyl (polymers **9** and **11**), the greater ϵ values are more detectable than in the corresponding *m*-methoxyphenyl-substituted copolymers (**8** and **10**). This presumably results from the favorable stereorelationship between phenyl ring methoxy substituents and/or alkyl side chains on Si atoms 1,3 to each other, and therefore the Si backbone bearing both *p*-methoxyphenyl groups (R_4, R_5) may adopt a more regular local conformation due to the lower steric hindrance.

The CD spectra of **7**–**11** (Figures 5 and 6), containing 20% chiral monomer units, exhibit a positive signed Cotton effects which almost trace the lowest energy backbone electronic transition (σ–σ^*) in the corresponding UV spectra. These results indicate that **7**–**11** adopt preferential screw-sense local helical backbone conformations and therefore that the introduction of only 20% chiral moieties is sufficient to induce cooperative helicity in the Si backbone. This is because the presence of enantiopure chiral "seeds" is able to induce a preferential helical screw-sense in even non-enantiopure-substituted backbone regions by the preferential stereorelationship between the enantiopure chiral side chains and their nearest neighbors.[11–13] This cooperative phenomenon[17] has been referred to as "sergeants and soldiers" to describe the nonlinear relation between the

Scheme 1. Structures of Poly(alkyl(methoxyphenyl)silane) Homo- and Copolymers 1–11



Polysilane	R_1	R_2
1	Me	*m*-position
2	Me	*p*-
3	Et	*m*-
4	Et	*p*-
5	*n*-Hex	*m*-
6	*n*-Hex	*p*-



	R_3	R_4	R_5
7	Me	*m*-	*m*-
8	Me	*p*-	*m*-
9	Me	*p*-	*p*-
10	*n*-Hex	*p*-	*m*-
11	*n*-Hex	*p*-	*p*-
12 (low Mw)	Me	*m*-	*p*-
13 (low Mw)	*n*-Hex	*m*-	*m*-
14 (low Mw)	*n*-Hex	*m*-	*p*-

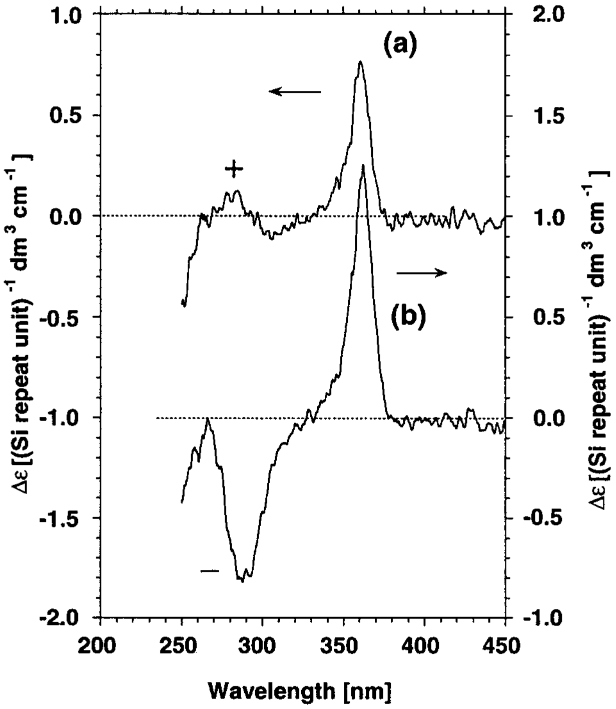


Figure 6. CD spectra of (a) **10** and (b) **11** in dilute THF solution at 20 °C.

specific optical rotation and the *ee* of chiral units in helical polythiophenes[18] and polyisocyanates[19] and has been also reported in dialkyl-, diaryl-,[12c] and alkylaryl-substituted[11h] polysilane systems. The positive CD sign in all achiral−chiral copolymers indicates that the Si conformations of **7**−**11** have a similar preferential helical screw-sense, regardless of the alkyl chain length and the methoxy group position. However, in the phenyl absorption region of the CD spectra, these were significant differences. When R_5 in the chiral monomer unit is the *m*-position, a positive CD sign is observed. In contrast, for *p*-methoxyphenyl-substituted (R_5) copolymers, a negative CD sign is exhibited. These results show that the position of methoxy groups on the phenyl ring may vary the phenyl side chain arrangements on the copolymer backbones without change of the preferential Si main-chain helical screw-sense. Presumably, the arrangement of methoxyphenyl pendants, either along the Si backbone screw-sense or opposite, may be determined by the lowest energy stereorelationship of either *m*- or *p*-methoxy groups so as to minimize the side-chain steric hindrance.

Conclusions

We succeeded in the synthesis and control of the optical and chiroptical characteristics and the global and local conformations in poly(alkyl(alkoxyphenyl)silane) homo- and copolymers by using the marked substituent effect in THF solution. Unfortunately, high molecular weight components for three copolymers, **12**, **13**, and **14**, were not obtained, presumably due to high steric hindrance. The poly(alkyl(alkoxyphenyl)silane) homopolymers **1**−**6** showed a typical absorption peak at around 340−360 nm due to delocalized σ-conjugation, which is also affected by phenyl $\pi \rightarrow \sigma^*$ mixing and electron-donating methoxy groups on the phenyl ring. The UV absorption properties of **1**−**6** in the Si backbone region were dramatically dependent on the alkyl side chain length, which might be also related to the polymer global conformation. Investigation of the viscosity index (α) of **1**−**6** indicated that the global backbone conformations of **1**−**6** might adopt a considerably shrunken random coil, a flexible coil, and a stiff extended structure, depending on the alkyl side chain length. However, when polysilanes **1**−**6** contained 20% enantiopure chiral monomer units, the copolymers exhibited optical activity due to the adoption of a preferential screw-sense local helical backbone conformation. In addition, the arrangement of the phenyl side pendants on the Si backbone, either along the Si backbone screw-sense or opposite, could be influenced by the substitution position of the methoxy group on the phenyl ring (*m*- or *p*-) in the chiral monomer units without change of the preferential Si main-chain helical screw-sense. We believe that these systematic investigations concerning marked substituent effects on the (chir)optical properties and conformations of poly(alkyl(methoxyphenyl)silane)s may open the intriguing possibility to design new functional polysilane materials.

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Supporting Information Available: The UV, FL and FL-A spectra of ethyl-substituted (**3**, **4**) and *n*-hexyl-*p*-methoxyphenyl-substituted (**6**) polysilanes in THF at room temperature, ^{13}C NMR of **1** and **2** in the methyl and phenyl regions, and UV, FL, and FL-A spectra of achiral−chiral polysilane copolymers (**7**−**11**). This material is available free of charge via the Internet at http://pubs.acs.org.

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