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Temperature Dependent CD Spectra of Poly(dihexylsilylene)s with Terminal Chiral Groups. Coupled Cotton Effects of Silicon σ Chains

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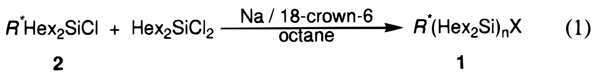
Much attention has been focused on the remarkable thermochromism of linear chain polysilanes.[1] The temperature dependence of the absorption spectrum of a linear polysilane is discontinuous; in a very narrow temperature range upon cooling, one absorption band disappears and a new band grows in at a longer wavelength region. Typically, while poly(dihexylsilylene) exhibits an intense absorption band at ca. 315 nm at room temperatures, upon cooling below ca −30 °C, the absorption bandwidth becomes much narrower and the maximum shifts to about 350 nm. The origin of the thermochromism is usually ascribed to the transition at low temperatures from a random coil to a nearly all-trans rod of the silicon backbone,[2] while Miller et al. have proposed that the red shift with decreasing temperature is caused by aggregation of polysilane chains.[3]

Recently, we have reported the synthesis and structure of linear eicosapropyldecasilanes with two chiral aralkyl substituents at the terminal silicon atoms; these oligosilanes show sharp and intense circular dichroism (CD) spectra at low temperatures due to the loose-helical chirality of the silicon chain with the dihedral angles of 165−170° (15/7 helix) for all the Si tetrads.[4] We report here that the helical chirality is induced in a linear polysilane polymer by introduction of the terminal point chirality. The observed coupled Cotton effects are explained by an exciton coupling model of two loose helical polysilane chromophores having 10−20 silicon atoms (segments) at a kink where σ conjugation in a linear polysilane chain is disconnected.

Poly(dihexylsilylene)s with terminal chiral groups, **1a** and **1b**, were synthesized by Wurtz couplings of dihexyldichlorosilane with *(R)*- (**2a**) and *(S)*-2-phenylpropyldihexylchlorosilane (**2b**), respectively,[5] using sodium dispersion in octane (eq 1). ^{1}H NMR spectra of **1a** and **1b** showed that about 18% of terminals in these two polymers were the chiral substituents.[6] These polymers were purified by reprecipitation with a mixture of toluene and 2-propanol and then by freeze-drying from a benzene solution. The structure of **1a** and **1b** was determined by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy.[6] The M_n values of **1a** and **1b** were determined to be 6000 and 5000, respectively, which correspond to ca. 30 and 25 dihexylsilylene units, respectively.



$$\underset{\mathbf{2}}{R^{*}\mathrm{Hex_2SiCl}} + \mathrm{Hex_2SiCl_2} \xrightarrow[\text{octane}]{\text{Na / 18-crown-6}} \underset{\mathbf{1}}{R^{*}(\mathrm{Hex_2Si})_n\mathrm{X}} \qquad (1)$$

1a: R^{*}- = *(R)*-$CH_3C^{*}H(Ph)CH_2$-, $Mn = 6.0 \times 10^3$, $Mw = 7.0 \times 10^3$, $P = 1.2$
1b: R^{*}- = *(S)*-$CH_3C^{*}H(Ph)CH_2$-, $Mn = 5.0 \times 10^3$, $Mw = 1.2 \times 10^4$, $P = 2.4$
2a: R^{*}- = *(R)*-$CH_3C^{*}H(Ph)CH_2$-
2b: R^{*}- = *(S)*-$CH_3C^{*}H(Ph)CH_2$-

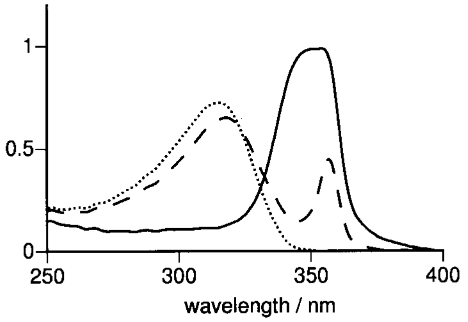


Figure 1. Temperature-dependent UV−vis spectra of **1b** (5.8×10^{-5} M per Si unit) in isopentane/methylcyclohexane (5/1): (···) at 233 K, (− −) at 223 K, and (—) at 213 K.

Figure 1 shows temperature-dependent UV−vis absorption spectra of poly(dihexylsilylene)s terminated by an *(S)*-2-phenylpropyl group (**1b**). Since the averaged molecular weight of **1b** is not high, the bandwidth at 213 K is rather wider than that of a poly(dihexylsilylene) with high molecular weight ($M_n > 10^5$). However, thermochromic behavior observed for **1b** is dramatic similarly to that for the high-molecular weight poly(dihexylsilylene). A similar temperature dependence of the UV−vis spectrum is observed for **1a**. There are no significant effects of terminal chiral groups on the thermochromic behavior of linear polysilanes.

Parts a and b of Figure 2 show temperature-dependent CD spectra of **1a** and **1b**, respectively. While no Cotton bands were observed at higher temperatures than 233 K, two intense CD bands of opposite sign were observed for **1a** and **1b** at low temperatures. The appearance temperature of the CD band (233 K) is parallel to the transition temperature in the UV−vis spectra. These features are similar to those found for linear decasilanes with terminal chiral groups,[4] indicating that the helical chirality of the polysilane chains of **1a** and **1b** is induced by the terminal chiral groups at lower temperatures. An interesting difference between decasilanes with terminal chiral substituents and the present polysilanes is the coupled Cotton effect in the latter, while the former shows the relatively simple positive and negative CD bands depending on the chirality of the terminal substituents. The coupled features of the Cotton bands of **1a** and **1b** are almost a mirror image of each other. The central points of these Cotton bands are completely the same as the $\lambda_{\max}$ of the polymers at the corresponding temperatures. The areas of the negative and positive Cotton bands are almost the same as each other.

All the features of the Cotton effects and their temperature dependence of **1a** are independent of the concentrations between 8.0×10^{-6} and 8.0×10^{-5} M per Si unit. The coupled Cotton effects observed in polysilanes **1a** and **1b** would be ascribed to the intramolecular origin at least in lower concentrations than 8.0×10^{-5} M per Si unit.

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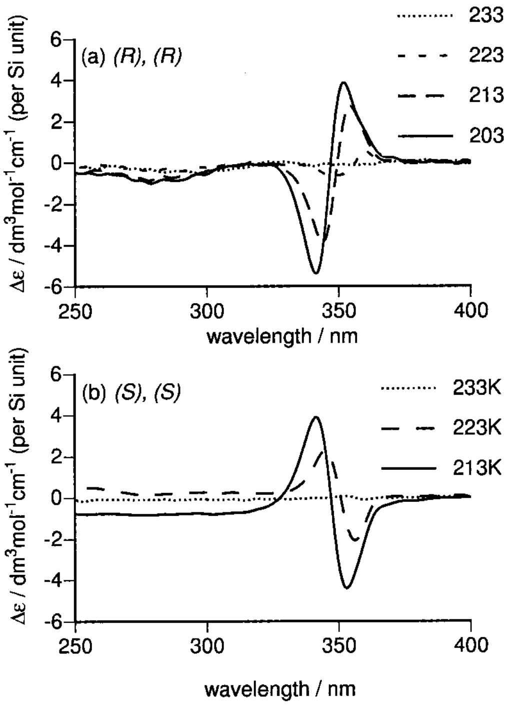

Figure 2. Temperature-dependent CD spectra of (a) **1a** (5.3×10^{-5} M per Si unit) and (b) **1b** (5.8×10^{-5} M per Si unit) in isopentane/methylcyclohexane (5/1). The $\Delta\epsilon$ values were not corrected for the content of chiral groups in a polymer.

Whereas two CD bands of opposite sign have been reported by Möller, Matyjaszewski, et al.,[7] and Fujiki,[8] the proposed origin is different from each other. Möller et al. ascribed the origin of the apparent coupled Cotton band in solution and in a thin film of poly(dipentylsilylene-*co*-di[(*S*)-2-methylbutylsilylene]) to the interaction between electronic transitions of the chirally ordered chromophoric units. On the other hand, weak positive and negative Cotton bands were observed for a solution of poly[(*S*)-2-methylbutyl−methylsilylene] by Fujiki, who has concluded that there are two parts with different helicities in a polymer molecule on the basis of the absorption-band selective photolysis.

In agreement with the explanation provided by Möller et al.,[7b] the coupled Cotton effects of **1a** and **1b** are explained by the exciton coupling between two polysilane chromophores. Polymers **1a** and **1b** have however chiral groups only at the terminals of the polymer chain, while regulation of the main-chain helicity is achieved by side-chain chiral substituents for the polymers of Möller[7] and Fujiki.[8] The following is a picture depicted for the coupled Cotton effects of our chiral polymers: The most stable conformation of the poly(dihexylsilylene) main chain will be a loose helical coil with the dihedral angles of ca. 170° for every Si tetrad as revealed by MM2 force field calculations for oligo(di-*n*-alkylsilylene)s[4,9] and by X-ray crystallographic analysis of 1,6-di[(*R*)-2-phenylpropyl]dodecapropylhexasilane.[4] Whereas the poly(dihexylsilylene) chain behaves as a random coil at higher temperatures, the population of the loose helical coil structure will increase with decreasing temperatures. According to the segment model for linear polysilanes,[1b] a polysilane chain at low temperatures will be divided into several loose-helical segments by kinks, where the σ conjugation in the main chain is disconnected; one to two dozen silicon atoms are supposed to exist in a segment and the dihedral angle of the Si−Si−Si−Si sequence at the kink is assumed to be 60 (gauche) or 90° (ortho).[9f,10] The chiral terminal groups in **1a** and **1b** regulate the hand of helicity of the loose-helical segments, which will in turn regulate the direction of twist at a kink as schematically represented in Figure 3. The MM2 force field calculations have confirmed that when the hand of helicity of a polysilane segment is fixed to the right-hand, the positive twist is more stable than the negative, and the left-handed helicity leads to the negative twist.

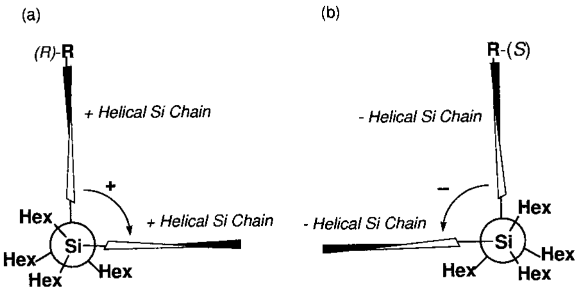

Figure 3. Schematic representation of regulation of the direction of twist at a kink of a poly(dihexylsilylene) with (a) terminal (*R*)- and (b) (*S*)-2-phenylpropyl groups.

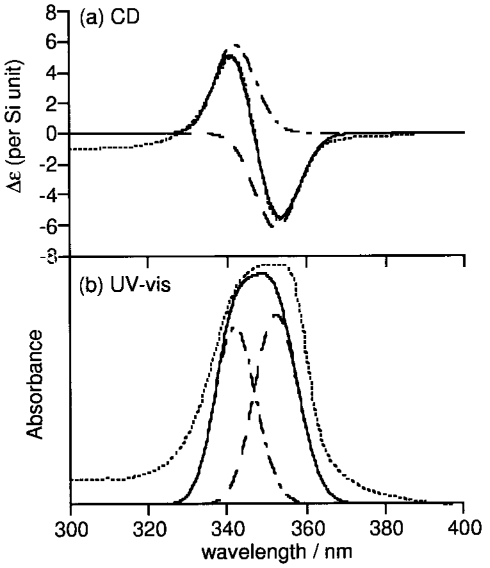

Figure 4. (a) Deconvolution of a CD spectrum of **1b**: (···) observed, (— —,—·—) component, and (—) reconstructed spectra. (b) Comparison of a UV−vis spectrum of **1b** observed at 213 K in isopentane/methylcyclohexane (5/1) and the reconstructed using the deconvoluted two CD bands. The discrepancy between experimental and calculated spectra would be ascribed to the low content of the chiral substituents in the polymer.

Interaction of two chromophores will cause the Davidov split of the transition energy. According to the theory of the interaction of two chromophores,[11,12] the absorption and CD spectra are classified into the following three patterns depending on the dihedral angle (θ) of the two transition dipoles: (a) when $\theta = 0°$, the transition of high energy side is forbidden by canceling out of the transition moments, (b) when $\theta = 180°$, the transition of the low energy side is forbidden, and (c) when $0° < \theta < 180°$, the two transitions are allowed. When $\theta = 90°$, the coupled Cotton bands of oposite sign and equal intensity will be observed in the CD spectrum, while the two bands will be overlapped in the absorption spectrum. The observed CD spectrum of **1b** is deconvoluted to two split bands ($\Delta\nu = 863$ cm^{-1}) with the same absolute intensity and half-bandwidth

(1040 cm^{-1}). As shown in Figure 4, using the deconvoluted two CD bands, the observed UV−vis spectrum is well reconstructed. The CD spectral features of **1a** and **1b** are compatible with case c ($\theta \approx 90°$).

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(5) Chiral chlorosilanes **2a** and **2b** were synthesized by the reactions of dihexylchlorosilane with *(R)*- and *(S)*-2-phenylpropylmagnesium chloride in THF^{4} followed by chlorination with CCl_4−dibenzoyl peroxide in overall yields of 53 and 30%, respectively. The Grignard reagents in ether were prepared by the reactions of magnesium and *(R)*- and *(S)*-2-phenylpropyl chlorides, which were obtained by the chlorination of the corresponding chiral alcohols with a thionyl chloride−pyridine reagent system; the *ee* values of the corresponding *(R)*- and *(S)*-alcohols were determined by using chiral HPLC columns (DAICEL CHIRALCEL-OB) to be 97% and 98%, respectively. Whereas neither **2a** nor **2b** was separated by any chiral columns we tried, the *ee* values for these chiral silicon compounds should be similar to those for the corresponding alcohols, because the synthetic routes do not give influence to the chirality. **2a:** ^{1}H NMR ($CDCl_3$) δ 0.52−0.76 (m, 4 H), 0.88−1.00 (m, 6 H), 1.20−1.52 (m, 22 H), 7.14−7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.1, 16.4, 16.9, 22.6, 22.87, 22.88, 26.21, 26.23, 31.43, 31.46, 32.8, 35.6, 126.2, 126.7, 128.5, 148.6; ^{29}Si NMR ($CDCl_3$) δ 31.9; MS *m/z* (rel intensity) 352 (M^+, 1), 267 (96), 233 (12), 225 (100), 183 (10), 149 (21), 151 (76), 105 (37); HRMS found = 352.2363 calcd for $C_{21}H_{37}Si_1Cl_1$, M, = 352.2351; $[\alpha]^{22}_{D} = +14.8$ (*c* 10.1, cyclohexane). **2b:** ^{1}H NMR ($CDCl_3$) δ 0.5−0.8 (m, 4 H), 0.9−1.0 (m, 6 H), 1.2−1.5 (m, 22 H), 7.13−7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.2, 16.4, 16.9, 22.6, 22.87, 22.88, 26.21, 26.23, 31.43, 31.46, 32.8, 35.6, 126.2, 126.7, 128.5, 148.6; ^{29}Si NMR ($CDCl_3$) δ 31.9; Mass *m/z* (rel intensity) 352 (M^+, 1), 267 (92), 233 (11), 225 (100), 183 (10), 149 (20), 151 (75), 105 (37); HRMS found = 352.2461, calcd for $C_{21}H_{37}Si_1Cl_1$, M, = 352.2351; $[\alpha]^{22}_{D} = -14.5$ (*c* 10.0, cyclohexane).

(6) Chiral polysilane **1a** was synthesized by a reductive coupling of a mixture of dihexyldichlorosilane (10 mmol) and **2a** (10 mmol) with sodium dispersion (35 mmol) in octane at reflux for 6 h. The insoluble part of the reaction mixture was removed by filtration and then the solvent was removed. Chiral polymer **1a** was separated by reprecipitation from a benzene-2-propanol mixture and then purified as white plastic solids by freeze-drying process. Chiral polysilane **1b** was synthesized by the same method as white plastic solids. **1a:** ^{1}H NMR ($CDCl_3$) δ 0.7−1.0 (m, 10 H), 1.2−1.6 (m, 16 H), [7.22−7.25 (m)]; ^{13}C NMR ($CDCl_3$) δ 14.2, 15.1, 22.9, 27.6, 31.9, 34.5, [125.7, 126.6, 128.2]; ^{29}Si NMR ($CDCl_3$) δ −25.0. Minor signals due to phenyl ring nuclei in a terminal chiral group are shown in brackets. $M_n = 6000$; $M_w = 7000$. **1b**: ^{1}H NMR ($CDCl_3$) δ 0.7−1.0 (m, 10 H), 1.1−1.5 (m, 16 H), [7.22−7.25 (m)]; ^{13}C NMR ($CDCl_3$) δ 14.1, 15.1, 22.9, 27.6, 31.9, 34.4, [125.7, 126.6, 128.2]; ^{29}Si NMR ($CDCl_3$) δ −25.0. Minor signals due to phenyl ring nuclei in a terminal chiral group are shown in brackets. $M_n = 5000$; $M_w = 12000$. The percent incorporation of the terminal chiral group in a polymer was calculated to be 18% for **1a** and **1b** based on the relative intensity of the hexyl α-methylene + methyl protons with that of phenyl protons.

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