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Optically Active Polysilane Homopolymer: Spectroscopic Evidence of Double-Screw-Sense Helical Segmentation and Reconstruction of a Single-Screw-Sense Helix by the "Cut-and-Paste" Technique

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Abstract: We have studied the skeleton conformation of optically active polysilane homopolymer, poly(methyl-((*S*)-2-methylbutyl)silane) (**1**), as a model of flexible chainlike polymers in solution, by means of various optical spectra (UV absorption, circular dichroism, fluorescence, fluorescence excitation, and fluorescence anisotropy), NMR spectra (^{13}C and ^{29}Si), intrinsic viscosity as a function of molecular weight of polymer, screw-sense-selective photolysis, and GPC analysis equipped with a photodiode array UV detector. From a comparison among its circular dichroism, UV absorption, fluorescence, and fluorescence excitation spectra, we concluded that both *P*-screw-sense, tight helical and *M*-screw-sense, loose helical segments coexist in the same chain of **1**—diastereomeric helical segment-like block structure. The screw-sense-selective photolysis suggests that segments responsible for *P*- and *M*-screw-senses consist of nine silicon atoms. On the basis of this conformational model, modified **1*** with almost a single *P*-screw-sense was reconstructed by the screw-sense-selective "cut-and-paste" procedure used for original **1**.

Introduction

A puzzling subject in macromolecular chemistry is the macro-meso-microscopic conformation of floppy chainlike polymers in solution.[1−3] In general, even when an enantiomerically pure monomer is polymerized, it is very difficult to identify whether the resulting polymer chain is a collection of diastereomeric segment-like conformations containing both *P*- and *M*-screw-senses or an enantiomerically pure conformation possessing only either *P*- or *M*-screw-sense. If an optically active polymer has a chromophoric main-chain absorption due to helical conformation, the screw-sense could be to some extent characterized more by its circular dichroism (CD) and UV−visible spectroscopies than less informative specific rotation. Until now, there have been several conformational studies using such chromophoric, optically active polymers induced by enantiomerically pure chiral pendants; polyacetylene,[4,5] polydiacetylene,[6] polythiophene,[7] polyisocyanide,[8,9] and polyisocyanate.[10,11] Nevertheless, due to the lack of fluorescence (FL) studies of these polymers, chiroptical analysis and discussion on the helicity, homogeneity, and rigidity of the chiral conformation have continued to attract a considerable amount of controversy.

Fortunately, chainlike polysilane, which is a new class of inorganic polymer consisting of both a chromophoric silicon skeleton and organic substituents, is known to exhibit conformation-sensitive, strong near-UV, and highly efficient FL bands, typically 3.1−4.4 eV, due to the σ conjugating backbone parallel to a chain axis.[12,13] The band calculation for an idealized polysilane with achiral, *trans-planar* conformation initially suggested that Si σ electrons in the chain can delocalize along the whole chain,[14,15] but later, many photophysical, light scattering, thermochromic, and theoretical studies showed that a Si σ electron in an actual polysilane chain is to some extent localized because of segment-like or wormlike conformation.[16−20] Apparent UV absorption is now recognized to originate from segment-like domains consisting of 10−20 silicon atoms or from a wormlike conformation. If an optically active polysilane were obtained, all FL and FL excitation (FLE) spectra, and FL anisotropy, which are linked with its CD and UV spectra, would enable us to draw a more advanced picture of the macro-meso-microscopic conformation. This is because the photoexcited energy above the optical band gap relaxes to the most energeti-

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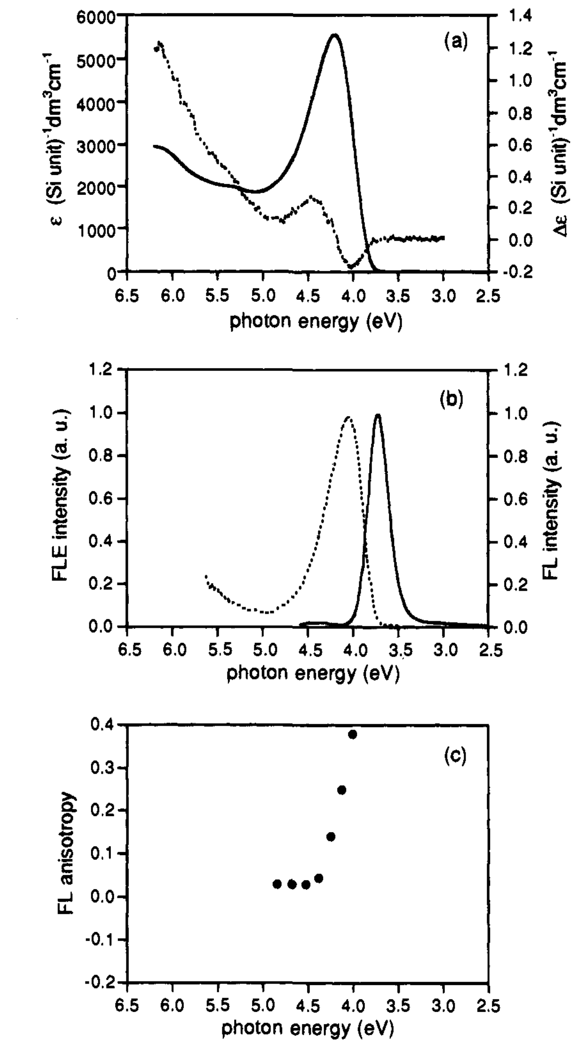
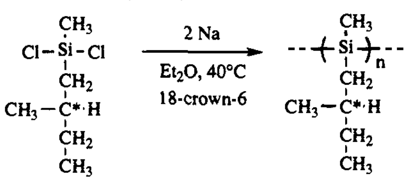


Figure 1. All spectral characteristics of **1** in isooctane at 20 °C: (a) UV (solid curve) and CD (dotted curve) spectra, (b) FL spectrum (solid curve) excited at 4.68 eV and FLE spectrum (dotted curve) monitored at 3.44 eV, and (c) the excitation energy dependence on the FL anisotropy (closed circles), corrected at the 3.72-eV FL and 4.06-eV UV−CD bands.

Scheme 1. Synthetic Scheme of Optically Active Polysilane Homopolymer, Poly(methyl((*S*)-2-methylbutyl)silane (**1**)



cally lowest domain or region and then can emit from it. Thus, the FL, UV, and CD spectral characteristics can be used as very powerful chiral probes in analyzing the helicity, homogeneity, and rigidity of the chiral conformation.

In a previous study, we showed an optically active polysilane, poly[methyl((*S*)-2-methylbutyl)silane] (**1**), takes on diastereomeric, segment-like conformation in a fluid solution by studying its UV, CD, and FL spectra and doing a screw-sense-selective Si−Si photoscission experiment.[21] In this paper, we will discuss an advanced conformational picture of polysilane **1** in more detail by means of various optical spectra (UV, CD, FL, FLE, and FL anisotropy), NMR spectra (^{13}C and ^{29}Si), intrinsic viscosity as a function of molecular weight of polymer, screw-sense-selective photolysis, and GPC analysis with a photodiode array UV detector. On the basis of this structure model, almost single-screw-sense helical **1*** was reconstructed by splicing of the Si−Si bonds—"cut-and-paste" technique—from **1**.

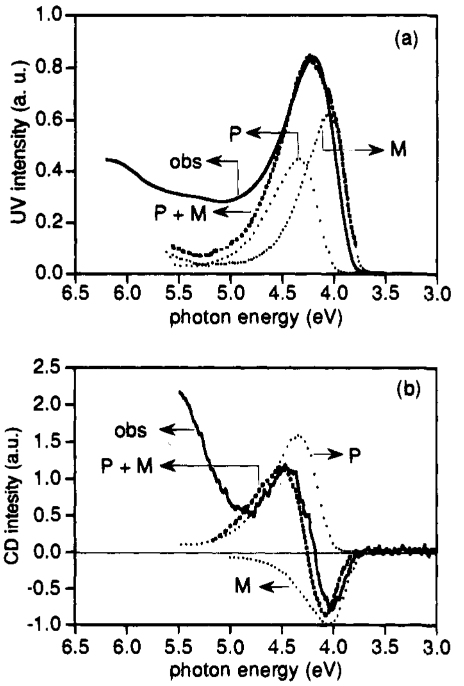


Figure 2. Simulation of the convoluted, deconvoluted, and actual spectral characteristics of **1**: (a) UV spectra and (b) CD spectra. Bold solid curves represent the observed UV and CD spectra, bold dotted curves are the simulated UV or CD spectra, and dotted curves stand for the deconvoluted UV and CD spectra, and *P* and *M* mean the helicity of Si sequence.

Results and Discussion

Identification of a Double-Screw-Sense, Diastereomeric, Broken Helix. Synthetic optically active polysilane homopolymer **1** is shown in Scheme 1. This polymer was easily obtained in excellent yield (see the Experimental Section), when a small amount of 18-crown-6 was added to the polymerization.[22]

Figures 1a, 1b, and 1c show the spectral characteristics of **1** in isooctane at 20 °C, UV, CD, FL, and FLE spectra, and the excitation energy dependence on the FL anisotropy. Polymer **1** exhibits bisigned Cotton CD bands—positive sign at 4.47 eV with a full-width at half-maximum (fwhm) of 0.67 eV and negative sign at 4.01 eV with fwhm of 0.26 eV—around broad UV absorption at 4.20 eV with fwhm of 0.67 eV assigned to the lowest Siσ−Siσ* transitions.[12,14] Polysilane **1** shows the narrow FL band at 3.72 eV with fwhm of 0.26 eV. The FL spectral profile does not match a mirror image of the 4.20-eV UV band but the 4.01-eV negative CD band. However, the fwhm value of the FLE spectrum, 0.47 eV, is about 2 times greater than that of the FL band and the peak value of the FLE spectrum, 4.06 eV, is slightly different from the extremum of the negative CD band. This discrepancy could be attributed to a mixing effect of two individual CD−UV components: The apparent bisigned CD bands showing the 4.01-eV and 4.47-eV extrema could deconvolute to 4.06-eV and 4.35-eV bands. As a result, the 4.35-eV CD band will be blue-shifted slightly and the 4.06-eV CD band wil be red-shifted slightly.

Figures 2a and 2b illustrate simulations of UV and CD spectra ranging from 3.5 to 5.0 eV using the PLE spectral profile for the 4.06-eV and 4.35-eV UV−CD bands. Assuming that the

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intensity of the positive CD band is 1.6 times greater than that of the negative CD band, the convoluted CD spectral shape qualitatively matches the actual bisigned CD bands within a small discrepancy on the extrema: The 4.35-eV CD band is blue-shifted by approximately 0.17 eV, whereas the 4.06−eV CD band is also blue-shifted by 0.03 eV. Similarly, if the intensity of the 4.06 UV band is 1.4 times greater than that of the 4.35-eV band, the convoluted UV profile becomes consistent with the observed UV band. Then, Kuhn's dissymmetry factor of the 4.35-eV band is evaluated to be about 2.2 times greater than that of the 4.06-eV band: the factor should increase as the helical angle increases.[23]

The FL anisotropy, corrected by the 3.72-eV FL and 4.06-eV UV−CD bands (*not* the 4.20-eV UV band), strongly depends on the excitation energy, varying from 0.03 to 0.38. The FL anisotropy is useful to estimate the relative arrangement between the transition dipole moments of emitting and absorbing domains. For example, there are three extreme cases: (a) when a transition dipole moment of emission is ideally consistent with that of absorption and these moments are distributed randomly in rigid media, the theoretical limit of PL anisotropy is expected to be 0.4, but (b) if emission and absorption dipoles are broken with an angle of 54°, the expected PL anisotropy becomes zero, and (c) when emission and absorption dipoles are bent perpendicularly, the PL anisotropy reaches −0.20. Fortunately, since the FL lifetime of polysilane is very short, typically 100−200 ps,[12] polymer conformation can be regarded to be frozen within its life time. If these simple pictures can be applied to polymer **1** in fluid solution, the observed photoexcited energy dependence on the FL anisotropy means that the transition dipole moment responsible for the 3.72-eV FL band is almost parallel to that for the 4.06-eV UV−CD band. However, the transition dipoles between the 4.35-eV UV−CD and 3.72-eV FL bands are broken at their junction with an angle of about 54°. As a result, the broad 4.20-eV broad UV band can be regarded as a collection of the 4.06-eV and 4.35-eV UV−CD domains and the photoexcited energy at 4.35 eV can effectively migrate to the nearest neighbor 4.06-eV domain and emit from it.

This mesoscopic view is also supported by the macroscopic relationship between intrinsic viscosity ($[\eta]$) and molecular weight (M) of **1**. Previous studies by light-scattering and $[\eta] - M^a$ measurements (a is viscosity index) indicate that most poly(dialkylsilane)s in solutions at room temperature are flexible and take on collective structures of relatively short approximately 30 Å long segments, or wormlike disordered structures.[12,19] The present $[\eta] - M^a$ measurement for **1** (in tetrahydrofuran at 30 °C) gives $a = 0.59$ ($M = 1000-500\,000$),[24] which is typical for flexible or coiled polymers.[25]

Figure 3 shows the Si−Si−Si−Si torsion angle dependence on the total steric energy of methyl((*S*)-2-methylbutyl)silane octamer terminated with *tert*-butyl groups for its isotactic and syndiotactic stereoisomers. The results were preliminaryly calculated by molecular mechanics (MM2) based on standard parameters with a Si−Si bond length of 2.332 Å and a Si−Si−Si bond angle of 111.3°.[26] Many local steric energy minima can be seen at torsion angles of 90°, 130°, 170°, and 210° in an isotactic configuration and similarly seen at 100°, 170°, 150°, and 200° in a syndiotactic configuration, with a moderately high barrier height of about 40−80 kcal/mol. The calculation results imply that *P*- and *M*-screw-sense diastereomeric helices coexist stably in the same chain with isotactic and syndiotactic configurations, beyond the thermal equilibrium state between diastereomeric domains. Although the relationship between helicity and CD band sign is still unclear, the respective *P*- and *M*-helical silicon domains are assumed to give positive and negative sign CD bands, because a *P*-screw-sense helical polysilane expected from preliminary MM2 calculations gives only positive sign CD spectrum experimentally.[24] The optical band gap of polysilane has been shown theoretically to increase as the helical torsion angle decreases.[27,28] If the calculations linked with the experimental evidence mentioned above can be applied to **1**, we can draw a more advanced structural model of **1**, as follows.

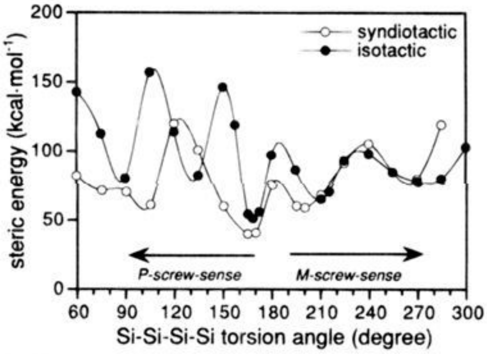

Figure 3. Torsion angle dependence on the steric energy of methyl((*S*)-2-methylbutyl)silane octamer with *tert*-butyl terminals for its isotactic and syndiotactic configurations.

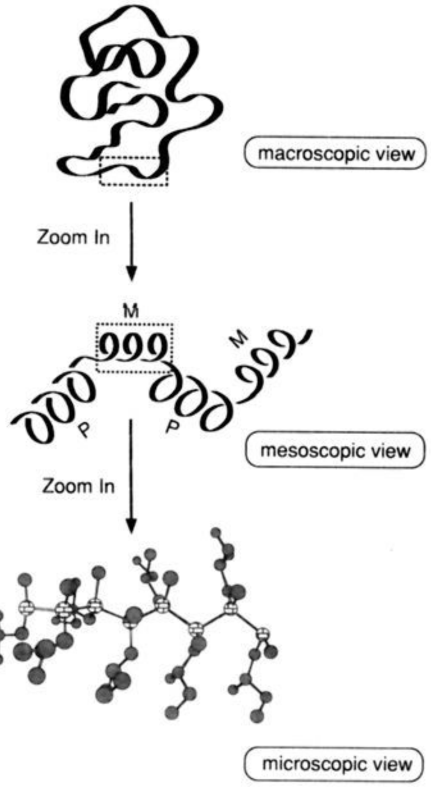

Figure 4. Macro-meso-microscopic views of **1** in solution. *P* and *M* represent the helicity of Si sequence.

Figure 4 illustrates the structural model of **1**. From the $[\eta] - M^{0.59}$ relationship, the chain of **1** has a coiled (or helical

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wormlike) conformation macroscopically. The FL anisotropy experiment shows that the chain is mesoscopically composed of both a *P*-screw-sense, tight helical domain with a 4.35-eV optical band gap and an *M*-screw-sense, loose helical domain with a 4.06-eV gap. The respective *P*-helical and *M*-helical domains are broken at their junction with an angle of about 54°. Moreover, the MM2 calculation shows that the domain is in the tightly wound helical or loosely wound helical state. This structural idea can be further confirmed by the following screw-sense-selective photolysis experiment, based on the prediction that these helical domains do not come from thermal equilibrium between diastereomeric states. As expected, to perform this experiment, the σ-electron of the Si skeleton should be electronically localized owing to the conformational structure.

Figures 5a–5d depict the change in UV and CD spectra of **1** photobleached at the positive and negative Cotton CD band in isooctane at 20 °C. When **1** was irradiated at the negative CD band for about 1 h, the CD band almost disappeared. The resulting positive CD band profile appeared at ~4.5 eV and resembled to the remaining, broad, blue-shifted UV band located at ~4.4 eV. Figure 5b shows the bleaching rate of the negative CD band is obviously faster than that of the positive one. Since the value of the weight-average degree of polymerization (P_w) decreased from 440 to only 9, the domain responsible for the positive CD band can be shown to have nine Si repeating numbers. On the other hand, when **1** was irradiated at the positive CD band, both the bisigned CD and UV bands were bleached completely within 2–3 h, producing very low molecular weight species. The intensities of the positive and negative CD bands decrease simultaneously. This means that the positive CD band irradiation breaks the Si–Si bonding of *P*- and *M*-screw-sense domains equally. As a result, although the positive CD band photolysis cannot give any information on the corresponding Si repeating numbers, we believe that the Si numbers of the positive CD band are almost the same as that of the negative CD band, judging from the fwhm value of the positive band: the fwhm value in the 4.47-eV CD band is similar to that in the 4.01-eV CD band. This is because the value of fwhm tends to increase gradually as the Si repeating numbers in the domain decrease.[27]

There are two possibe explanations of these changes in these CD and UV spectra. Polymeric diastereomers—both *P*- and *M*-screw-sense helical chains—individually exist in solution, and also the polymer chain consists of *P*- and *M*-screw-sense helical domains. The GPC analysis equipped with a photodiode array UV detector strongly agrees with the latter possibility. This is because the features of broad UV absorption and apparent UV peak position of **1** are independent of molecular weight and the **1** that was photodecomposed at the negative CD band gave only oligomers showing blue-shifted UV band at ~4.5 eV.

Reconstruction of a *P*-Screw-Sense Helix by the Screw-Sense-Selective "Cut-and-Paste" Technique. On the basis of the meso-microscopic conformational model, we tried to reconstruct a *P*-screw-sense helical polysilane showing only positive Cotton CD band (**1***) by the following "cut-and-paste" procedure used for original **1**. The basic concept is shown schematically in Figure 6. The "cut-and-paste" procedure consists of three steps: (i) photoscission of **1** (P_w = 440) was performed at the negative Cotton CD band in CCl_4 at 23 °C using a CD spectropolarimeter, (ii) Si-skeleton telomers terminated with Si–Cl bonds (P_w = 9 by GPC and δ = +32.5 ppm (broad, weak) by ^{29}Si-NMR in $CDCl_3$) were formed which showed a positive Cotton CD band at ~4.5 eV, and (iii) after removal of volatile material in a vacuum at about 200 °C, the resulting colorless oil was recondensed with Na in hot toluene with a small amount of 15-crown-5 (the color of the Na surface changed from gray to purple during this reaction). The unpurified colorless oil was **1*** with P_w = 30.

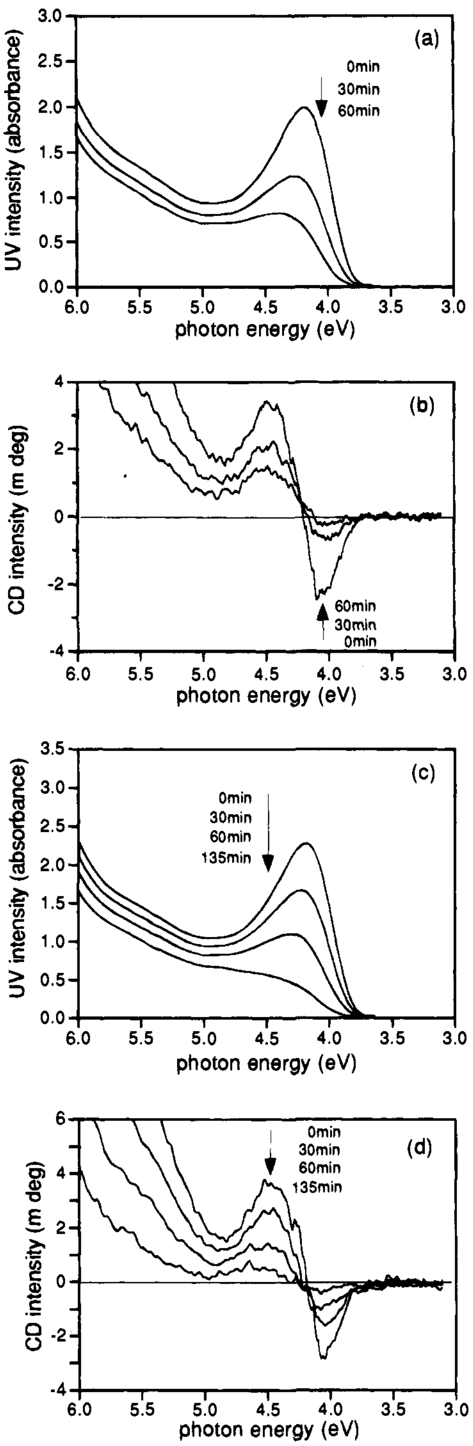

Figure 5. Change in UV and CD spectra of **1** as a function of photolysis time in isooctane at 25 °C, $[Si]_0 = 4 \times 10^{-4}$ (Si unit)$^{-1}$ dm^3 cm^{-1}, and slit width of spectropolarimeter of 2 nm: (a) UV spectra and (b) CD spectra for photolysis at the 4.0-eV negative CD band; (c) UV spectra and (d) CD spectra for photolysis at the 4.5-eV positive CD band.

Figures 7a and 7b compare the change in UV and CD spectra of original polymer **1** and reconstructed polymer **1***. These results show that **1*** possesses mainly a positive Cotton CD band at 4.5 eV associated with a very weak negative CD band at 4.0 eV, and also Siσ–Siσ* skeleton absorption near 4.4 eV. Figures 8a and 8b contrast the change in solution ^{13}C- and ^{29}Si-NMR spectra of **1** and **1***. Both **1** and **1*** show three well-resolved ^{13}C peaks consisting of two prominent and one faint

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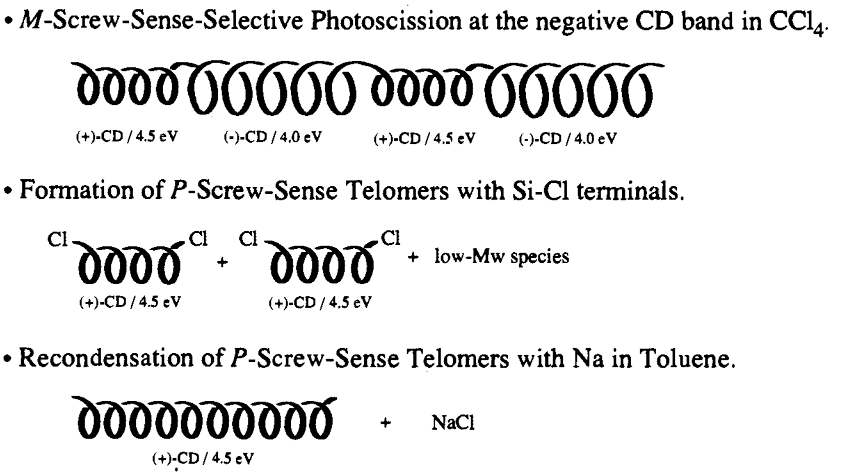

Figure 6. Key ideas for the reconstruction of *P*-screw-sense helical polymer **1*** by a "cut-and-paste" procedure featuring (i) *M*-screw-sense-selective photolysis in CCl_4, (ii) formation of *P*-screw-sense telomers with Si—Cl terminals, and (iii) Na-mediated recondensation of the telomers in hot toluene.

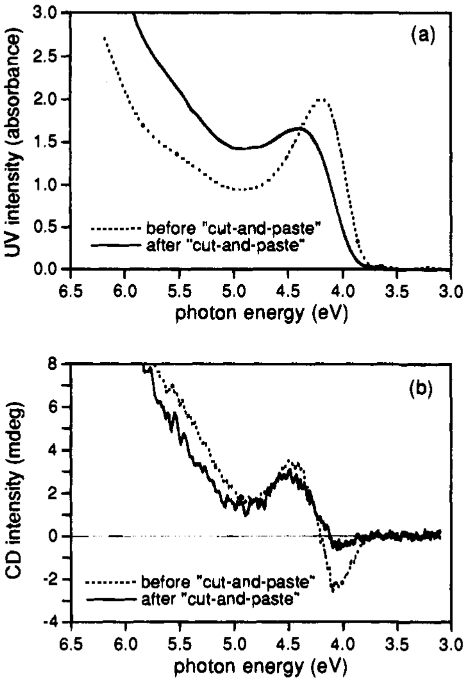

Figure 7. Change in UV and CD spectra of **1** and **1*** in isooctane at 20 °C: (a) UV spectra and (b) CD spectra. (Since as-prepared, oily samples of **1*** were measured without purification, exact UV and CD intensities are unclear.)

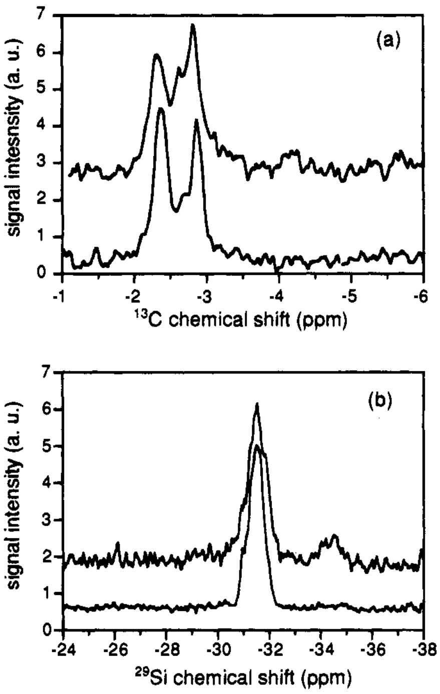

Figure 8. Change in ^{13}C-NMR (75.43 MHz, $CDCl_3$, 20 °C) and ^{29}Si-NMR (59.59 MHz, $CDCl_3$, 20°C) spectra of **1** and **1***: (a) ^{13}C-NMR spectra of **1** (top) and **1*** (bottom) and (b) ^{29}Si-NMR spectra of **1** (top) and **1*** (bottom).

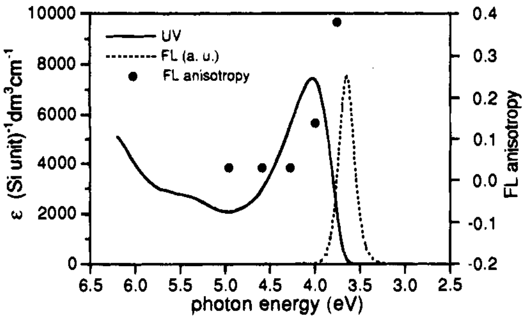

Figure 9. Spectral characteristics of **3** in isooctane at 20 °C. UV spectrum (solid curve), FL spectrum (dotted curve) excited at 4.68 eV, and the excitation energy dependence on the FL anisotropy (closed circles), corrected at 3.65-eV FL and 4.04-eV UV bands.

proportion located at −2.10, −2.34, and −2.49 ppm. These peaks could be assigned to CH_3 carbon attached to Si skeleton, that possibly relates to *P*-screw-sense and *M*-screw-sense domains and/or four possible triad stereochemical sequences (*mm*, *mr*, *rm*, and *rr*) in the chain. After the "cut-and-paste" treatment of **1**, the portion of the three ^{13}C peaks of **1*** becomes completely different from those of original **1**. In contrast, solution ^{29}Si-NMR spectra of **1** and **1*** seem to be insensitive to the change of configuration and/or microscopic conformation in the Si skeleton.

All features of the UV and FL spectra and excitation energy dependence of FL anisotropy in **1** are very similar to those in most optically inactive, floppy polysilanes reported so far, such as poly(di-*n*-hexylsilane) (**2**) and poly(methyl(*n*-propyl)silane) (**3**).[12] The respective [η]-M^a measurements (in tetrahydrofuran at 30°C) for **2** and **3** give a = 0.74 (10 000 < M< 500 000) and 0.62 (5 000 < M< 50 000) as **1**.[24] For a comparison, the spectral characteristics of **3** in isooctane at 20 °C are shown in Figure 9. Apparently, the spectral features of the UV and FL spectral profiles—*not* the mirror-image relationship between the UV and FL band—and the marked excitation energy dependence on the FL anisotropy in **3** are almost identical to those in **1**. If

1 is regarded as a good model of a "snap shot" of such flexible polysilanes (and mobile chainlike polymers), these polymers are assumed to take on collective mixed structures composed of *P*- and *M*-screw-sense, loose and tight helical domains existing in the same backbone, resulting from thermodynamic equilibrium, as illustrated in Figure 4.

Conclusion

In conclusion, we observed spectroscopically the skeleton segmentation of an optically active organopolysilane homopolymer (**1**) bearing a chiral substituent as a model of flexible polymers in solution. From a comparison of its circular dichroism, UV absorption, fluorescence and fluorescence excitation spectra, we concluded that both *P*-screw-sense, tight helical and *M*-screw-sense, loose helical segments coexist in the same chain, namely diastereomeric helical segment-like block polymer. From a photolysis experiment, the segment chain length of positive Cotton CD band was estimated to be nine silicon atoms. Helical polymer **1*** having an almost positive Cotton CD band was reconstructed from the original helical polymer **1** showing bisigned CD bands, by the screw-sense-selective "cut-and-paste" procedure of a silicon skeleton. Finally, the FL spectral characteristics combined with the corresponding UV and CD spectra arising from chiral mainchain were found to be very powerful chiral probes in analyzing the helicity, homogeneity, and rigidity of a skeleton.

Experimental Section

Analysis. Circular dichroism (CD) and UV spectral measurements and photolysis experiments were carried out using at a JASCO J720 spectropolarimeter. Fluorescence and fluorescence excitation spectra and excitation energy dependence of the fluorescence were measured using a Hitachi F850 spectrofluorometer. FT-NMR spectra (^{13}C and ^{29}Si) were measured by a Varian Unity-300 NMR spectrometer with an electronically switchable four-nuclei (^{1}H, ^{13}C, ^{29}Si, ^{19}F) probe. Molecular weight, polydispersity, and in-line absorption spectra of the polysilanes were measured by a Shimadzu A10 series HPLC apparatus with a JASCO Multi340 photodiode array UV–vis–near infrared detector, deaerated unit, UV–vis detector, and double-plunger pump: Shodex mixed gel KF80M as the GPC column and tetrahydrofuran as eluent at 40 °C. Specific rotation was determined by a JASCO DIP340. Differential scanning calorimetric (DSC) measurement was carried out at the Toray Research Center (Shiga, Japan) using a Seiko 220C DSC instrument with a heating rate of 10 deg/min. Viscosity–molecular weight of the polymer was also measured using universal calibration curve and analyzed at the Toray Research Center using a Waters 1500 GPC instrument equipped with a Viscotec H502a viscometer and differential refractometer: Shodex KF-806L and Tohso GMH$_{XL}$ as GPC columns, tetrahydrofuran as eluant at 30 °C.

Preparation of Methyl((*S*)-2-methylbutyl)dichlorosilane. To a mixture of 125 mL of dry tetrahydrofuran (Dotite) and Mg turnings 9.5 g (0.41 mol) with a small amount of iodine, 4.5 g (0.03 mol) of (*S*)-2-methylbutyl bromide (Aldrich) was added dropwise. After the iodine color disappeared, 36.0 g (0.34 mol) of (*S*)-2-methylbutyl chloride (Tokyo Kasei) was added dropwise to the moderately refluxing, stirred solution. The reaction mixture was allowed to react for several hours. To a mixture of 80 g (0.54 mol) of methyltrichlorosilane (Shin-Etshu Silicon) and 150 mL of dry diethyl ether (Dotite), fresh Grignard reagent was added dropwise from a dropping funnel at 40 °C and allowed to react overnight. After adding about 1 L of *n*-hexane to the reaction mixture, a yellow clear solution containing monomer was collected by reduced filtration. After the solvent and unreacted trichlorosilane was roughly evaporated under reduced pressure (~200 mmHg), the resultant mixture was carefully distilled. The yield was 20.5 g (30%): $[\alpha]^{23}_{D}$ 12.6 (neat); bp 78–79 °C/20 mmHg; ^{29}Si-NMR (59.59 MHz, $CDCl_3$, $(CH_3)_4Si$ as reference) 32.51 ppm; ^{13}C-NMR (75.43 MHz, $CDCl_3$, $(CH_3)_4Si$ as reference) 32.23, 30.27, 29.39, 21.70, 11.15, 6.38 ppm.

Preparation of Polymer 1. To a mixture of 50 mL of dry diethyl ether (Dotite), 1.9 g of Na dispersion (30% in toluene, Janssen), and 0.05 g (0.2 mmol) of 18-crown-6 (Aldrich) in an Ar atmosphere was added 2.05 g (11 mmol) of methyl((*S*)-2-methylbutyl)dichlorosilane dropwise at 40 °C. The reaction mixture was allowed to react for 12 h. The reaction mixture was cooled to room temperature and passed through a 5-μm PTFE filter under Ar gas. Then the filtrate was poured into deaerated cold ethanol at about −40 to −60 °C, and the resulting white precipitate was quickly collected by centrifugation and dried at 60 °C in a vacuum overnight. The yield of colorless polymer **1** was 0.45 g (36%).

^{29}Si-NMR (59.59 MHz, $CDCl_3$, $(CH_3)_4Si$ as reference) gave an unresolved peak with many shoulders centered at −31.5 ppm. ^{13}C-NMR (75.43 MHz, $CDCl_3$, $(CH_3)_4Si$ as reference) showed three well-resolved peaks at −2.10, −2.34, and −2.49 ppm for the $SiCH_3$ group. Other ^{13}C NMR signals were tentatively assigned as follows; 11.41 ppm for $\mathit{C}H_3CH_2CH(CH_3)CH_2Si$, 22.35, 22.67, 22.88, 23.18 ppm for $CH_3CH_2CH(\mathit{C}H_3)CH_2Si$, and 33.41 ppm for $CH_3\mathit{C}H_2\mathit{C}H(CH_3)CH_2Si$. The weight-average of molecular weight (M_w) and the polydispersity were 5.06 × 10^4 and 3.1, respectively, based on a calibration of polystyrene standards, at 40 °C using tetrahydrofuran as eluent. The M_w corresponds to about 440 Si repeating units. The glass transition temperature was −17.7 °C by DSC measurement.