Macromolecules **2004,** *37,* 4321−4324 **4321**

Thermodriven Chiroptical Switching of a Polysilane Thin Film

Sun-Young Kim,[†] Michiya Fujiki,*[,‡] Akihiro Ohira,[‡] Giseop Kwak,[‡] and Yusuke Kawakami[†]

Graduate School of Materials Science,
Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan,
and Graduate School of Materials Science,
Nara Institute of Science and Technology,
8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Received January 30, 2004
Revised Manuscript Received March 10, 2004

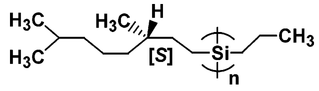
Introduction

The design and development of smart materials for a chiroptical switch and memory at the molecular level is a challenging issue for miniaturization in materials science and engineering.[1] The basic requirement for a switching system is the bistable states of a molecule, which can be rapidly interconverted by an external stimulus.[2] In many synthetic polymers containing enantiopure chiral side chains (e.g., polyisocyanates,[3] polyacetylenes,[4] polythiophenes,[5] polyfluorenes,[6] and polysilanes[7]), their backbone adopts a preferential screw sense, *P* (plus, right-handed) or *M* (minus, left-handed). Such polymers are promising candidates as molecular chiroptical switches because of their reversible bistable states, which can be assigned as either "+1 and −1" through the helix−helix transition or "+1 and 0" through the helix−coil transition. The conformational change of polymers can be detected in the absorption region of the polymer chains by circular dichroism (CD).

Although many studies have been established concerning the switching of the helical conformation in solution, they might be preliminary. A focus on the transition, either in bulk thin film or in a polymer matrix, is needed from a practical viewpoint.[8] The glass transition temperature (T_g) is the critical factor in the design of the chiroptical switch in the solid state. Below T_g, the segmental motion of the polymer chain is frozen. Even above T_g, the response time would depend on the difference between T_g and the conformational transition temperature (T_c). Thus, the polymer having a relatively low T_g may be a good candidate for practical application.

Polysilanes exhibit a unique electronic absorption band in the UV region ranging from 300 to 400 nm, which is assigned to the $\sigma-\sigma^*$ electronic transition of the delocalized electrons along the silicon backbone.[9] The conformation of polysilanes strongly depends on the substituent species, and the position of λ_{max} in the UV absorption reflects their conformation in connection with the degree of conjugation. Especially, in polysilanes having enantiopure chiral side chains, their helical sense can be characterized by the Kuhn dissymmetry ratio (g_{abs}), $\Delta\epsilon/\epsilon$, because the CD spectra generally show a similar profile to the UV absorption band, and the value of g_{abs} gives the quantitative information associated with the degree of a preferential screw sense.[10] Polysilanes possessing relevant enantiopure chiral side chains will, therefore, be successful candidates for a chiroptical switch and memory at the molecular level.

Scheme 1. Chemical Structure of PDMOPS



In this work, we report on the helix−coil transition of poly{(*S*)-3,7-dimethyloctyl-*n*-propylsilane}, PDMOPS, in solution as well as in the solid state and on the feasibility of its application as chiroptical switches and memory.

Experimental Section

General. The solid film was prepared by casting from an isooctane solution (0.5 mg/mL). The UV and CD absorption spectra of the thin film were recorded simultaneously on a JASCO J-725 spectropolarimeter equipped with a liquid nitrogen controller in a cryostat, ranging from 20 to −60 °C. The scanning condition was as follows: a scanning rate of 500 nm/min, a bandwidth of 1 nm, a response time of 1 s, and a single accumulation. ^{13}C and ^{29}Si NMR spectra were measured in $CDCl_3$ with a JEOL EX-400 spectrometer. Optical rotation at the Na D line was measured with a JASCO P-1020 polarimeter using quartz cells with a path length of 10 and 100 mm for the monomer and the polymer, respectively, at room temperature. The weight-average molecular weight (M_w) and number-average molecular weight (M_n) were determined using gel permeation chromatography (Shimadzu A10 instruments, Plgel 10 μm MIXED-B as a column and HPLC-grade tetrahydrofuran as an eluent) at 40 °C, based on a calibration with polystyrene standards. The differential scanning calorimetric (DSC) analysis was performed on a Seiko EXSTAR6000/DSC6200 instrument with a heating rate of 10.0 °C/min.

Materials. (*S*)-3,7-Dimethyloctyl-*n*-propyldichlorosilane: (*S*)-3,7-Dimethyloctyl bromide (28.4 g, 130 mmol) was reacted with Mg (3.8 g, 156 mmol) in dry tetrahydrofuran (100 mL) at 50 °C. The Grignard reagent was added to *n*-propyltrichlorosilane (23.0 g, 130 mmol) in dry tetrahydrofuran (100 mL) at 50 °C. The salts were removed by filtration from the reaction mixture. The crude product was purified by distillation to give the desired monomer as a colorless liquid in 45% yield; bp = 139−141 °C (10 mmHg). ^{13}C NMR in $CDCl_3$ (ppm): 16.14, 17.21, 17.54, 19.06, 22.58, 22.60, 22.70, 24.71, 27.95, 29.10, 34.77, 36.43, 39.27. ^{29}Si NMR in $CDCl_3$ (ppm): 33.88, $[\alpha]_D^{24} = 2.00°$ (neat).

Poly{(*S*)-3,7-dimethyloctyl-*n*-propylsilane}, PDMOPS: Freshly distilled monomer (10 g, 35.3 mmol) was added dropwise to 1.71 g (74.2 mmol) of Na metal suspended in 30 mL of refluxing toluene while vigorously stirring under a nitrogen atmosphere. After 2 h, the reaction mixture was cooled to room temperature, and 100 mL of dry toluene was added to reduce solution viscosity. Stirring was continued for a further 30 min. The reaction mixture was passed through a 2 μm PTFE filter under nitrogen gas pressure. To the clear filtrate, 2-propanol and ethanol as precipitating solvents were carefully added. Several portions of the white precipitates were collected by centrifugation and dried in vacuo at 80 °C. Yield = 5.5%, fraction 1: M_w = 1 700 000 and M_w/M_n = 1.79, fraction 2: M_w = 330 000 and M_w/M_n = 1.87. ^{29}Si NMR in $CDCl_3$ (ppm): −24.6, $[\alpha]_D^{22} = 10.5°$ (1.0 mg/mL, in isooctane), d = 0.884 g/cm^3.

Results and Discussion

In Dilute Solution. From the ^{29}Si NMR line width ($\Delta\nu_{1/2}$) of around 26 Hz in $CDCl_3$ at 30 °C,[11] PDMOPS is expected to adopt a fairly flexible conformation with freely rotating Si−Si bonds in solution. This coillike

---

[†] Japan Advanced Institute of Science and Technology.
[‡] Nara Institute of Science and Technology.
* To whom correspondence should be addressed: FAX +81-743-72-6049; Tel +81-743-72-6040; e-mail fujikim@ms.aist-nara.ac.jp.

10.1021/ma049807s CCC: $27.50

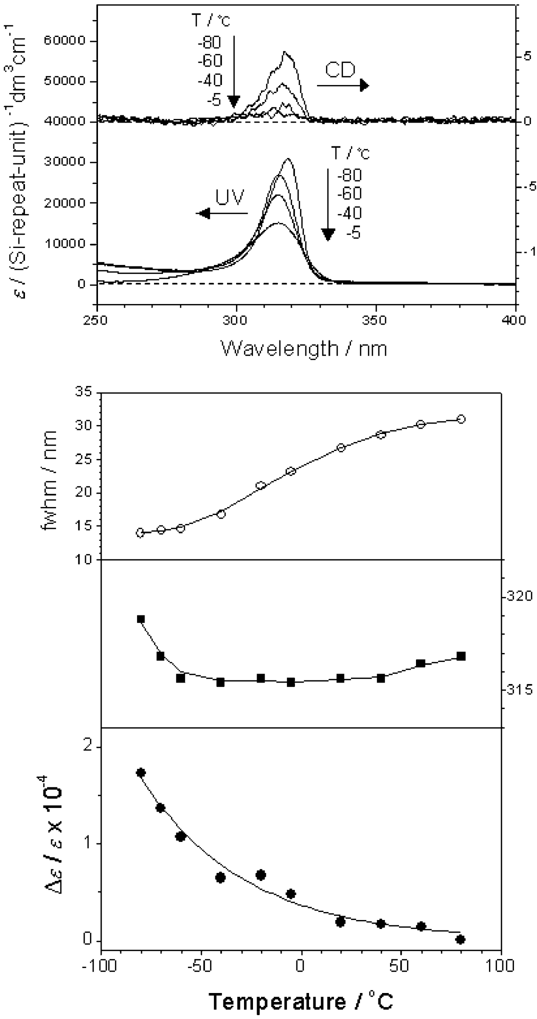


Figure 1. For PDMOPS in isooctane (a) UV and CD absorption spectra and (b) g_{abs} ($\Delta\epsilon/\epsilon$), λ_{max}, and fwhm as a function of temperature; $M_w = 330\ 000$, $M_w/M_n = 1.87$, concentration $= 7.35 \times 10^{-5}$ M.

shape can also be explained by weak broad UV absorption ($\epsilon = 13\ 000$ (Si repeat unit)$^{-1}$ dm^3 cm^{-1} and fwhm = 26.6 nm) in isooctane at 20 °C (Figure 1). The flexibility of PDMOPS may be attributed to the ineffective packing between γ-branching 3,7-dimethyloctyl and relatively short n-propyl groups around the Si backbone at room temperature. PDMOPS showed no detectable Cotton effect, despite enantiopure chiral side chains, in isooctane at 20 °C, which means there was no selectivity between left and right circularly polarized light in the absorption. However, PDMOPS underwent the transition from a coillike conformation ($\epsilon = 11\ 300$ (Si repeat unit)$^{-1}$ dm^3 cm^{-1} and $g_{abs} = 0$ at 80 °C) to a stable helical conformation ($\epsilon = 30\ 700$ (Si repeat unit)$^{-1}$ dm^3 cm^{-1} and $g_{abs} = 1.72 \times 10^{-4}$ at -80 °C) having a preferential screw sense as the temperature decreased. The fwhm (full width at half-maximum) of UV absorption peak, the degree of the inhomogeneity of chromophores, became narrower upon cooling with a relatively strong temperature dependence between 20 and -40 °C, which means the degree of freedom in the rotation of Si$-$Si bonds falls off with decreasing temperature and the main chain of PDMOPS maintains its rigidity. Despite the chain rigidity formed to some extent, PDMOPS seems to include many helical reversals in their main chain, showing the relatively small value of g_{abs} ($\Delta\epsilon/\epsilon = 0.65 \times 10^{-4}$) at -40 °C. However, the Kuhn dissymmetry ratio increased steeply with strong dependence on the decreasing temperature below -40 °C. Concurrently with the increasing g_{abs}, the λ_{max} shifted to a longer wavelength. This red shift of the UV absorption peak suggests the elongation of the effective conjugation length through the excess of single-screw helical conformation formed by the movement and/or disappearance of helical reversals.

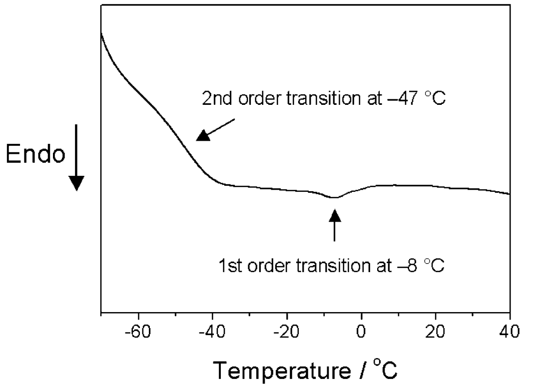


Figure 2. DSC thermogram of PDMOPS obtained upon second heating with heating rate of 10 °C /min.

In Thin Solid Film. The thermal behavior of PDMOPS was analyzed in the bulk state using differential scanning calorimetry (DSC). The DSC thermogram displayed a second-order transition at -47 °C and a first-order transition at -8 °C corresponding to the glass transition and the helix$-$coil transition, respectively (Figure 2). The heat flow ($\Delta H = 0.08$ J/g) for the helix$-$coil transition in PDMOPS was relatively small, but highly reproducible.[12]

Figure 3 shows the UV and CD spectra of the PDMOPS film cast from an isooctane solution at a second heating run (heating/cooling rates of around 1$-$5 °C/min).[13] Although there was no detectable CD absorption at 20 °C, PDMOPS showed the strong Cotton effect at -40 °C,[14] indicating a coil-to-helix transition of PDMOPS in the solid state with decreasing temperature. This transition can be well correlated with DSC results. The positive Cotton effect could result from a single polymer chain because of the similarity between the UV and CD absorption profiles, and no bisignate CD signal attributable to exciton coupling between polymer chains at even -60 °C. Although PDMOPS showed the strong Cotton effect at low temperature in solution as well as in the solid state, the global conformations of polymer chains in both states may be significantly different. PDMOPS in solution is assumed to adopt a stiff global conformation with a relatively long persistence length and an excess of single screw sense through the transition at low temperature.[7c] However, the entire conformation of the polymer chains in the solid state appeared to be difficult to change with decreasing temperature, even above their glass transition temperature, because of the excluded volume of other chains and the chain entanglements.

The helix$-$coil transition in the thin solid film can be explained by some parameters, such as fwhm, λ_{max} and ΔOD/OD (OD = optical density, ΔOD/OD is defined as $2(\mathrm{OD_L} - \mathrm{OD_R})/(\mathrm{OD_L} + \mathrm{OD_R})$). The fwhm of the UV absorption band became narrower when decreasing the temperature from 20 to -40 °C and turned out to be constant below -40 °C, which means the homogeneity of chromophores was induced according to the decreas-

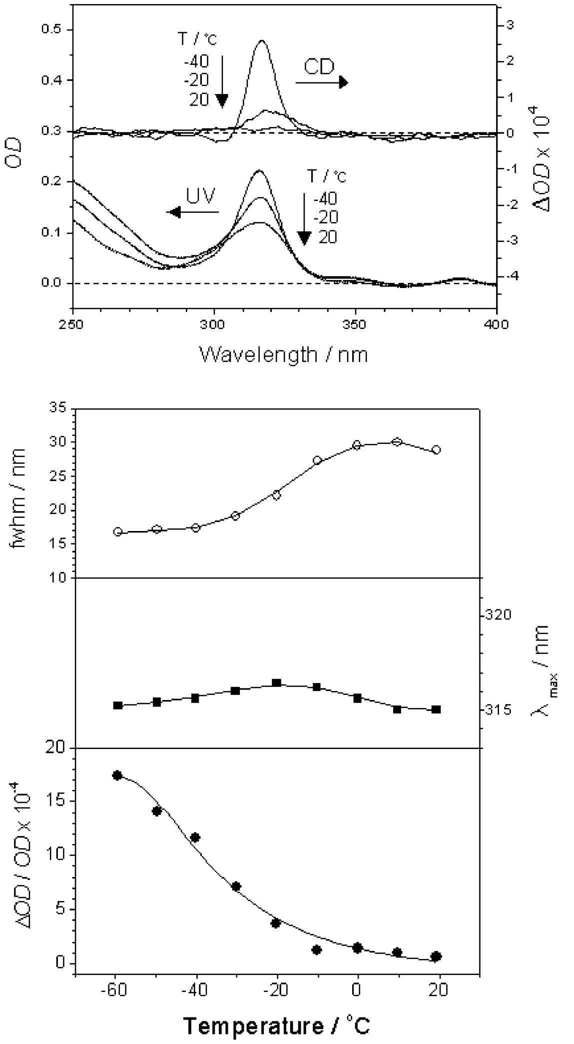


Figure 3. For PDMOPS in thin film (a) UV and CD absorption spectra and (b) ΔOD/OD, $\lambda_{\max}$, and fwhm as a function of temperature; M_w = 330 000, M_w/M_n = 1.87.

ing degree of freedom in the rotation of Si−Si bonds like in solution. The $\lambda_{\max}$ shifted slightly to a longer wavelength with decreasing temperature from 20 to −20 °C and shifted to a shorter wavelength below −20 °C. In solution, the increase of the $\Delta\epsilon/\epsilon$ was accompanied by the red shift of $\lambda_{\max}$, while in the thin film, the ΔOD/OD increased simultaneously with the slight blue shift of $\lambda_{\max}$. This phenomenon in the solid state may be attributed to the difficulty in change of global conformation when decreasing the temperature as mentioned above. Therefore, it is likely that the Cotton effect in the solid state was induced through the movement and/or disappearance of helical reversal within the localized segments and that this induction of helix was not accompanied by the change of the global conformation.

The helix−coil transition of PDMOPS in the solid state was highly reversible with changing temperature. Figure 4 shows the dependence of ΔOD/OD on the repeating cycle of the temperature in the range from −20 to 20 °C. The values of ΔOD/OD at each temperature were relatively reproducible, which could be attributed to the low T_g. Suggested from the small heat flow of only 0.08 J/g, weak van der Waals interaction among the side chains is presumably responsible for the reversible chiroptical switching between optically active and inactive states.

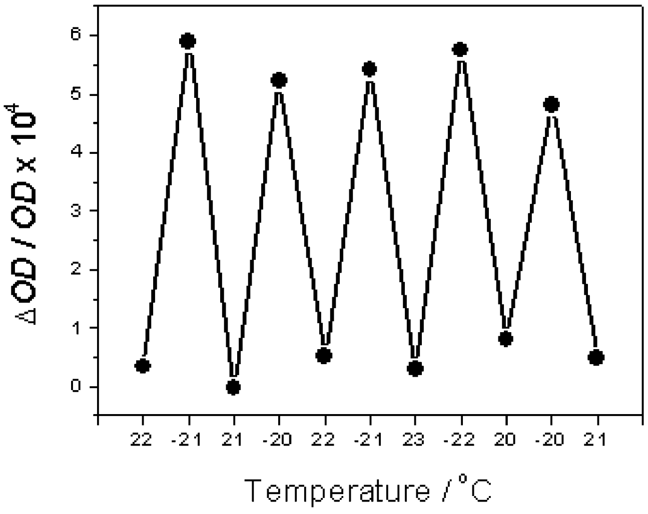


Figure 4. Dependence of ΔOD/OD on the repeatedly changing temperature between −20 and 20 °C.

Conclusion

We demonstrated the thermodriven helix−coil transition of PDMOPS in solution as well as in the solid state. The transition temperature in the solid state was 50 °C higher than that in solution. The helix−coil transition in solution accompanied the elongation of the conjugation length through the global conformational change. However, in the solid state, the change in such global conformation could hardly occur during the helix−coil transition and the observed Cotton effect was ascribed to the induced helix in the local segments. The helix−coil transition in the solid state was highly reversible and can be applicable in the switching system assigned as "+1 and 0".

Acknowledgment. This research was partially supported by a grant from the Japanese Society of Promotion of Science (JSPS). S.Y.K. thanks the Ministry of Education, Science, Sports, Culture of Japan (Monbukagakusho) for the Scholarship.

References and Notes

(1) (a) Hopfield, J. J.; Onuchic, J. N.; Beratan, D. N. *Science* **1988**, *241*, 817. (b) Ball, P.; Garwin, L. *Nature (London)* **1992**, *355*, 761. (c) Wilson, E. K. *Chem. Eng. News* **2003**, *81*, 27.

(2) (a) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789. (b) Raymo, F. M.; Giordani, S. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4941. (c) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature (London)* **2002**, *420*, 759. (d) Lahann, J.; Mitragotri, S.; Tran, T.-N.; Kaido, H.; Sundaram, J.; Choi, I.-S.; Hoffer, S.; Somorjai, G. A.; Langer, R. *Science* **2003**, *299*, 371.

(3) (a) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860. (b) Müller, M.; Zentel, R. *Macromolecules* **1996**, *29*, 1609.

(4) (a) Yashima, E.; Maeda, K.; Okamoto, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8895. (b) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature (London)* **1999**, *399*, 449.

(5) (a) Zhang, Z.-B.; Fujiki, M.; Motonaga, M.; Nakashima, H.; Torimitsu, K.; Tang, H.-Z. *Macromolecules* **2002**, *35*, 941. (b) Langeveld-Voss, B. M. W.; Christiaans, M. P. T.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1998**, *31*, 6702.

(6) (a) Oda, M.; Meskers, S. C. J.; Nothofer, H. G.; Scherf, U.; Neher, D. *Synth. Met.* **2000**, *111−112*, 575. (b) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365.

(7) (a) Fujiki, M.; Koe, J. R.; Motonaga, M.; Nakashima, H.; Terao, K.; Teramoto, A. *J. Am. Chem. Soc.* **2001**, *123*, 6253.

(b) Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336. (c) Terao, K.; Terao, Y.; Teramoto, A.; Nakamura, N.; Fujiki, M.; Sato, T. *Macromolecules* **2001**, *34*, 4519. (d) Terao, K.; Terao, Y.; Teramoto, A.; Nakamura, N.; Fujiki, M.; Sato, T. *Macromolecules* **2001**, *34*, 6519. (e) Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 669.

(8) (a) Muellers, B. T.; Park, J.-W.; Brookhart, M. S.; Green, M. M. *Macromolecules* **2001**, *34*, 527. (b) Mayer, S.; Zentel, R. *Macromol. Rapid Commun.* **2000**, *21*, 927. (c) Catellani, M.; Luzzati, S.; Bertini, F.; Bolognesl, A.; Lebon, F.; Longhi, G.; Abbate, S.; Famulari, A.; Meille, S. V. *Chem. Mater.* **2002**, *14*, 4819. (d) Roux, C.; Leclere, M. *Macromolecules* **1992**, *25*, 2141. (e) Watanabe, J.; Okamoto, S.; Satoh, K.; Sakajiri, K.; Furuya, H.; Abe, A. *Macromolecules* **1996**, *29*, 7084.

(9) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (b) Michl, J.; West, R. In *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications*; Kluwer: Dordrecht, 2000; Chapter 18.

(10) (a) Dekkers, H. P. J. M. In *Circular Dichroism: Principles and Applications*, 2nd ed.; Berova, N., Nakanishi, K., Woody, R. W., Eds.; Wiley-VCH: New York, 2000; Chapter 7. (b) Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539.

(11) Kim, S.-Y.; Saxena, A.; Kwak, G.; Fujiki, M.; Kawakami, Y. *Chem. Commun.* **2004**, 538.

(12) Yuan, C.-H.; West, R. *Macromolecules* **1994**, *27*, 629.

(13) The film thickness (around 80 nm) was calculated from the density of PDMOPS, the film area on the quartz plate, and the film weight. The film weight was obtained from the concentration of solution and the amount of solution used for the cast film. The root-mean-square roughness (R_{rms}) was less than 10 nm from the AFM measurement.

(14) A rotation of the quartz plate did not bring about any detectable difference in the UV and CD absorption spectra, which means the PDMOPS film cast onto quartz was isotropic with respect to the axis of observation.

MA049807S