Solvent and Temperature Effects on the Chiral Aggregation of Poly(alkylarylsilane)s Bearing Remote Chiral Groups

Hiroshi Nakashima,[†,‡] Michiya Fujiki,*[,†,‡] Julian R. Koe,[†,‡] and Masao Motonaga[‡]

Contribution from NTT (Nippon Telegraph and Telephone Corporation), Basic Research Laboratories, 3-1 Wakamiya, Morinosato, Atsugi, Kanagawa 243-0198, Japan, and CREST-JST (Japan Science and Technology Corporation), 4-1-8 Hon-cho, Kawaguchi, Saitama 332-0012, Japan

Received March 10, 2000

Abstract: Novel switchable chiroptical characteristics of poly(alkylarylsilane) microaggregates, controllable by the choice of good/poor solvent ratio (solvent polarity), solvent addition order, and sample temperature are described. The formation of stable chiral aggregates depends critically on the polysilane structure and stereochemistry. Poly[*n*-hexyl-(*p*-(*S*)-2-methylbutoxyphenyl)silane] (**1**), optically inactive in molecularly dispersed THF solution due to the existence of dynamically equivalent amounts of right (*P*)- and left (*M*)-handed screw sense helical main chain domains, shows a marked bisignate CD signal due to the formation of chiral aggregates in good/poor cosolvent systems. The sign and magnitude of the CD signals are dependent on solvent polarity, solvent addition order, and thermal effects. The less sterically hindered poly[methyl-(*p*-(*S*)-2-methylbutoxyphenyl)silane] (**2**) exhibits a weak, bisignate, nonswitchable CD signal in only the toluene/acetonitrile system, and no CD signals are evident in pure toluene or THF due to masking of the helicity. In contrast, although the even less sterically hindered, less polar poly[methyl-(*m*-(*S*)-2-methylbutoxyphenyl)-silane] (**3**) does show optical activity in pure THF or toluene (negative CD signal at 310 nm), the CD signal disappears on formation of aggregates in good/poor cosolvent systems.

Introduction

The search for a molecular-based chiroptical switch and memory that operates with efficiency, reversibility, and permanency is currently a challenging issue in the area of information science and technology.[1] Synthetic helical chromophoric polymers adopting bistable chiroptical states, *P* (plus, right-handed) and *M* (minus, left-handed) screw sense segments in a helical backbone, are potential candidates for such application in chiroptical devices in the UV/visible region, if a rapid chiroptical change between the bistable states driven by an external stimulus occurs. These synthetic polymers 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 side chains. In many synthetic polymers containing enantiopure chiral side chain groups, e.g., polypeptides,[2] polymethacrylates,[3] polyisocyanides,[4] polyisocyanates,[5] polyacetylenes,[6] and polysilanes,[7−10] the backbone may adopt a preferential screw sense helical conformation due to the side chain interactions. However, *P*−*M* helical inversion between

---

[†] NTT.

[‡] CREST-JST.

(1) (a) Koumura N.; Zijlstra, R. W.; van Delden, R. A.; Harada, N.; Feringa, B. L. *Nature* **1999**, *401*, 152. (b) Boiadjiev, S. E.; Lightner, D. A. *J. Am. Chem. Soc.* **2000**, *122*, 378. (c) Zahn S.; Canary, J. W. *Angew. Chem., Int. Ed*. **1998**, *37*, 305. (d) Castellano, R. K.; Nuckolls, C.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1999**, *121*, 11156. (e) Inoue, Y.; Ikeda, H.; Kaneda, M.; Sumimura, T.; Everitt, S. R. L.; Wada, T. *J. Am. Chem. Soc.* **2000**, *122*, 406. (f) Borovkov, V. V.; Lintuluoto, J. M.; Fujiki, M.; Inoue, Y. *J. Am. Chem. Soc.* **2000**, *122*, 4403. (g) Gin, M. S.; Yokozawa, T.; Prince, R. B.; Moore, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 2643. (h) Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, N. *J. Am. Chem. Soc*. **1997**, *119*, 7605. (i) Agati, G.; McDonagh A. F. *J. Am. Chem. Soc*. **1995**, *117*, 4425. (j) Masatoshi, S.; Takeda, M.; Fukushima, S.; Kurokawa, T. *Appl. Opt.* **1998**, *37*, 7523. (k) Yamaguchi, T.; Uchida K.; Irie M. *J. Am. Chem. Soc*. **1997**, *119*, 6066. (l) Clair, J. J. L. *Angew. Chem., Int. Ed*. **1999**, *38*, 3045. (m) Schmiedar, R.; Hübner, G.; Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed*. **1999**, *38*, 3528. (n) Weber, C.; Rustemeyer, F.; Dürr, H. *Adv. Mater.* **1998**, 10, 1348. (o) Yashima, E.; Maeda, K.; Okamoto, Y. *Nature* **1999**, *399*, 449.

(2) (a) Reidy, M. P.; Green, M. M. *Macromolecules* **1990**, *23*, 4225. (b) Yue, S.; Berry, G. C.; Green, M. M. *Macromolecules* **1996**, *29*, 6175.

(3) (a) Nakano, T.; Okamoto, Y.; Hatada, K. *J. Am. Chem. Soc*. **1992**, *114*, 1318. (b) Okamoto, Y.; Suzuki, K.; Ohta, K.; Hatada, K.; Yuki, H. *J. Am. Chem. Soc*. **1979**, *101*, 4763.

(4) (a) Ramos, E.; Bosch, J.; Serrano, J. L.; Sierra, T.; Veciana, J. *J. Am. Chem. Soc*. **1996**, *118*, 4703. (b) Kamer, P. C. J.; Nolte, R. J. M.; Drenth, W. *J. Am. Chem. Soc*. **1988**, *110*, 6818. (c) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, *23*, 11. (d) Green, M. M.; Gross, R. A.; Schilling, F. C.; Zero, K.; Crosby, C., III *Macromolecules* **1988**, *21*, 1839. (e) Takei, F.; Yanai, K.; Onitsuka, K.; Takahashi, S. *Angew. Chem., Int. Ed*. **1996**, *35*, 1554.

(5) (a) Maxein, G.; Zentel, R. *Macromolecules* **1995**, *28*, 8438. (b) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860. (c) Jha, S. K.; Cheon, K.-S.; Green, M. M.; Selinger, J. V. *J. Am. Chem. Soc*. **1999**, *121*, 1665. (d) Cheon, K.-S.; Selinger, J. V.; Green, M. M. *Angew. Chem., Int. Ed*. **2000**, *39*, 1482. (e) Maeda, K.; Okamoto, Y. *Macromolecules* **1998**, *31*, 5164. (f) Maeda, K.; Okamoto, Y. *Macromolecules* **1998**, *31*, 1046.

(6) (a) Yashima, E.; Maeda, Y.; Okamoto, Y. *J. Am. Chem. Soc*. **1998**, *120*, 8895. (b) Yashima, E.; Huang, S.; Matsushima, T.; Okamoto, Y. *Macromolecules* **1995**, *28*, 4184.

(7) (a) Koe, J. R.; Fujiki, M.; Nakashima, H. *J. Am. Chem. Soc*. **1999**, *121*, 9734. (b) Terunuma, D.; Nagumo, K.; Kamata, N.; Matsuoka, K.; Kuzuhara, H. *Chem. Lett*. **1998**, 681. (c) Fujiki, M.; Toyoda, S.; Yuan, C.-H.; Takigawa, H. *Chirality* **1998**, *10*, 667. (d) Obata, K.; Kabuto, C.; Kira, M. *J. Am. Chem. Soc*. **1997**, *119*, 11345. (e) Fujiki, M. *J. Am. Chem. Soc*. **1994**, *116*, 6017. (f) Frey, H.; Möller, M.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 1814. (g) Matyjaszewski, K. *J. Inorg. Organomet. Polym*. **1992**, *2*, 5.

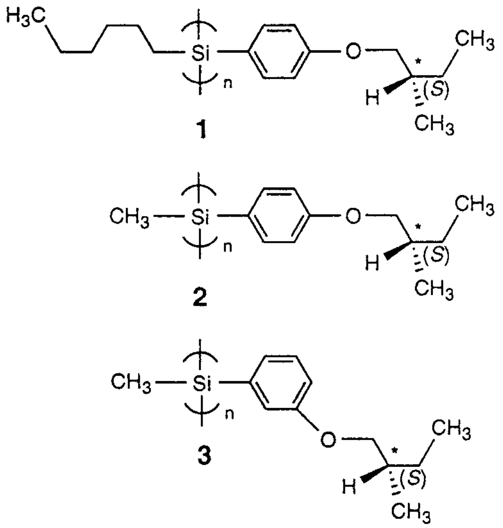
(8) Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336.

(9) Koe, J. R.; Fujiki, M.; Motonaga, M.; Nakashima, H. *Chem. Commun.* **2000**, 389.

(10) (a) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359. (b) Harrah, L. A.; Zeigler, J. M. *Macromolecules* **1987**, *20*, 601. (c) West, R. *J. Organomet. Chem.* **1986**, *300*, 327. (d) Cleij, T. J.; King, J. K.; Jenneskens, L. W. *Macromolecules* **2000**, *33*, 89.

10.1021/ja000869h CCC: $20.00

Scheme 1. Chemical Structures of Polysilanes **1**−**3**



the two energetically accessible, opposite screw sense states of the main chain is seldom observed in dilute solution.

Recently, we found that two types of helical polysilanes containing enantiopure chiral side chains, poly(dialkylsilane)s[8] and poly(diarylsilane)s,[9] may exhibit a thermo-driven circular dichroism (CD) switching effect due to such a $P-M$ transition in the molecularly dispersed solution state. Poly(alkylalkoxyphenylsilane)s bearing enantiopure chiral substituents in the *para* position on the phenyl ring, however, in contrast to poly(dialkylsilane)s or poly(diarylsilane)s, were optically inactive in dilute solution due to the presence of equivalent amounts of P and M helical segments.[11]

On the other hand, it has been well established for several π-conjugated polymers bearing chiral side chains that, even though the polymer may be optically inactive in the single molecule state, optical activity may be observed in a microaggregated form due to greater ordering. Interestingly, aggregation of chiral polymers into chiral superstructures influences the optical and chiroptical properties of conjugated systems considerably. For instance, the sign and magnitude of the bisignate CD signal switching of polythiophene[12] or poly(*l*-aspartate)[13] aggregates in response to the cooling rate and/or temperature of the film or the ratio of good/poor cosolvents have been described. Concerning the analysis of optically active aggregates and supramolecularly ordered systems in conjugated polymers, several optical measurement techniques are available: absorption, optical rotation (rotation of the plane of linearly polarized light on passing through the sample), and CD spectroscopy, which is perhaps the most appropriate technique, since it permits the direct analysis of chiral backbone physical and electronic structures.

Here we describe our investigations of the higher order chiral structural changes of poly(alkylalkoxyphenylsilane) **1**−**3** (Scheme 1) aggregates and their unique CD properties in detail, experimentally addressing such factors as solvent polarity, thermal effects, and the polysilane chemical structures. We also demonstrate the novel switchable CD effects of **1** aggregates, controllable by the addition order and ratio of good/poor solvents, as well as sample temperature.

Table 1. Synthesis and Optical Characterization [a]of Polysilanes **1**−**3**

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

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

Results and Discussion

Chiroptical Properties of Polysilane Aggregates in THF/Methanol Cosolvents. The CD spectra of polysilane **1**, bearing an enantiopure (*S*)-2-methylbutoxy group in the *para* position on the phenyl ring, show no CD signal in dilute THF solution (5×10^{-5} mol·L^{-1}) even at −80 °C,[11] because **1** contains dynamically equivalent amounts of *P*- and *M*-handed screw sense helical main chain domains in solution, a phenomenon reported for several polymers.[14,15]

However, THF solutions of **1** containing methanol (a poor solvent) show a marked bisignate CD signal. Figure 1a−c shows the UV and CD spectra and CD intensities of **1** aggregates at various THF/methanol ratios at 20 °C, respectively. When methanol was gradually added into the THF solution (Method I),[16] no CD band could be detected in mixtures containing less than 30% methanol by volume. At a THF/methanol ratio of 60%/40%,[7c] a well-resolved bisignate CD signal[12,15] was observed (Figure 1b; positive at $\lambda_{ext} = 370$ nm, negative at $\lambda_{ext} = 353$ nm; a positive Cotton effect). Interestingly, this positive Cotton effect in excess THF became a negative Cotton effect above 60% methanol. The crossover point occurred at ca. 50%/50% THF/methanol (Figure 1c). The bisignate CD intensities changed continuously with increasing methanol concentration. The UV spectra of **1** aggregates with increasing methanol gradually shifted to longer wavelength and tailing, due to precipitation of the polysilane, was observed (Figure 1a). The results of the CD analysis of **1** aggregates show clearly that **1**, while optically inactive in a good solvent, formed optically active chiral aggregates in a good/poor mixed solvent system. In addition, the chirality of the aggregates was switchable by the solvent polarity, as has also been reported for a polythiophene.[12] The bisignate nature of CD spectra is considered to be characteristic of exciton coupling between closely situated transition dipole moments on neighboring polymer segments in chiral configurations.[7c,12,15,17] In chiral aggregates, such coupling could result either intramolecularly, by interaction between adjacent helical segments, or intermolecularly, by interaction between adjacent helical main chains, such as occurs

---

[11] Nakashima, H.; Fujiki, M.; Koe, J. R. *Macromolecules* **1999**, *32*, 7707.

[12] (a) Lermo, E. R.; Langeveld-Voss, B. M. W.; Janssen, R. A. J.; Meijer, E. W. *Chem. Commun.* **1999**, 791. (b) Langeveld-Voss, B. M. W.; Waterval, R. J. M.; Janssen, R. A. J.; Meijer, E. W. *Macromolecules* **1999**, *32*, 227. (c) Bouman, M. M.; Meijer, E. W. *Adv. Mater.* **1995**, 7, 385. (d) Bidan, G.; Guillerez, S.; Sorokin, V. *Adv. Mater.* **1996**, 8, 157.

[13] (a) Watanabe, J.; Okamoto, S.; Abe, A. *Liq. Cryst.* **1993**, *15*, 259. (b) Watanabe, J.; Okamoto, S.; Satoh, K.; Sakajiri, K.; Furuya, H.; Abe, A. *Macromolecules* **1996**, *29*, 7084.

[14] (a) Green, M. M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Selinger, R. L. B.; Selinger, J. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3138. (b) Green, M. M.; Garetz, B. A.; Munoz, B.; Chang, H.-P. *J. Am. Chem. Soc.* **1995**, *117*, 4181. (c) Green, M. M.; Khatri, C.; Peterson, N. C. *J. Am. Chem. Soc.* **1993**, *115*, 4941. (d) Lifson, S.; Felder, C E.; Green M. M. *Macromolecules* **1992**, *25*, 4142.

[15] (a) Fiesel, R.; Scherf, U. *Acta Polym.* **1998**, *49*, 445. (b) Peeters, E.; Delmotte, A.; Janssen, R. A.; Meijer, E. W. *Adv. Mater.* **1997**, *9*, 493.

[16] Solvent addition order methods are assigned as follows: Method I, a poor solvent was gradually added into a good solvent solution containing **1**; Method II, a good solvent solution containing **1** was gradually added into a poor solvent.

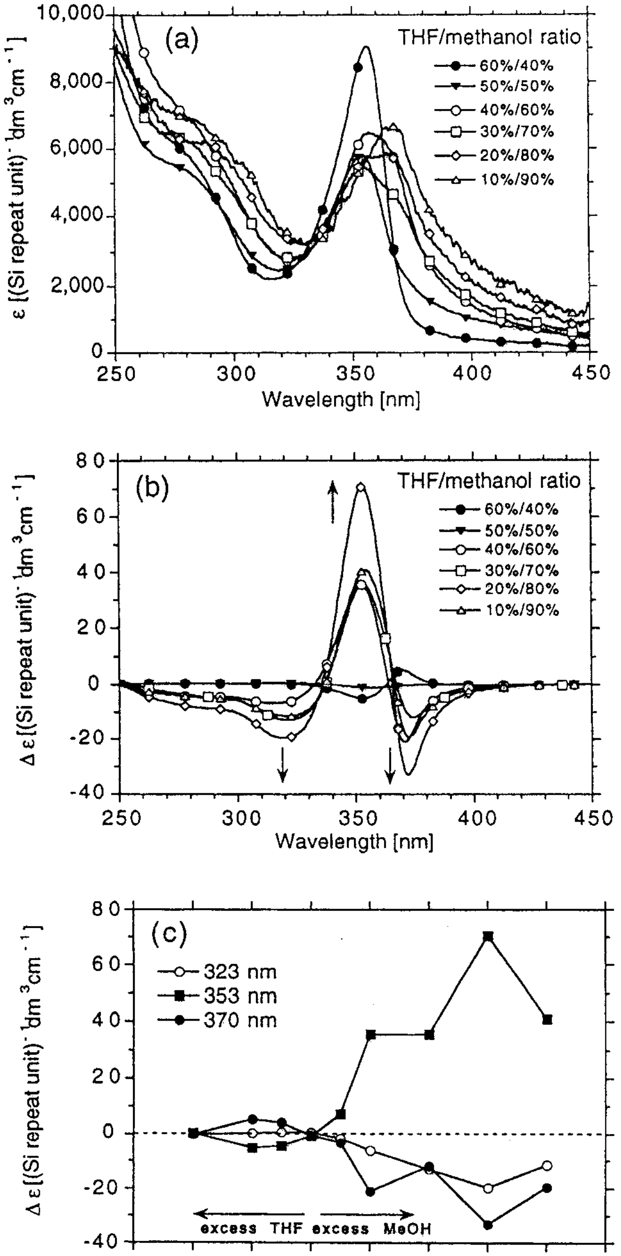


Figure 1. (a) UV−vis spectra, (b) CD spectra, and (c) plot of CD intensities of **1** aggregates prepared by Method I at various THF/methanol ratios at 20 °C.

in the packing of cholesteric liquid crystals.[2,13] To determine the more likely origin, we measured the CD spectra of the chiral aggregates after filtration using several different pore size filters. After filtration through a 5 μm filter, the CD profiles were similar to those of unfiltered samples (though the CD intensities decreased slightly), while after 0.5 μm filtration, no CD signals were evident. The particle size of the aggregates may thus be estimated to be greater than 0.5 μm, indicating that the CD effects are induced by an *intermolecular* chiral configuration of polymers.

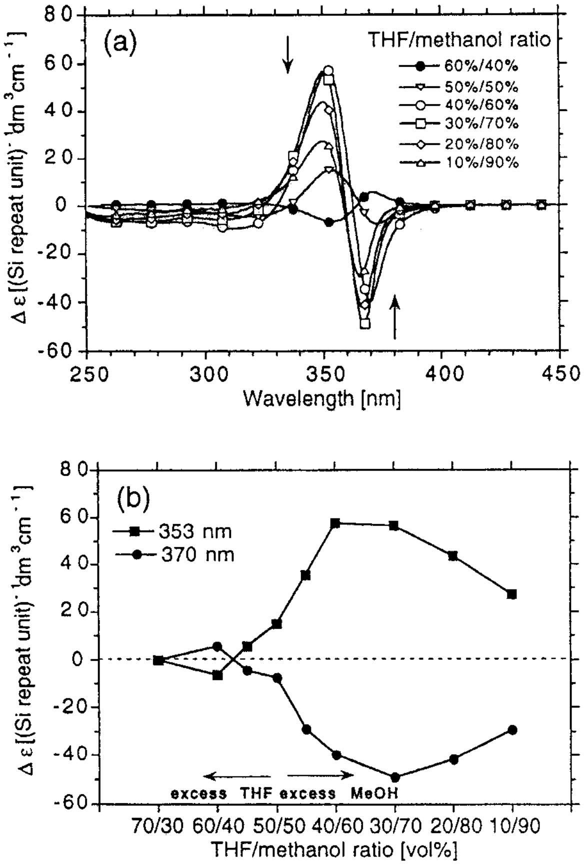


Figure 2. (a) CD spectra and (b) plot of CD intensities of **1** aggregates prepared by Method II at various THF/methanol ratios at 20 °C.

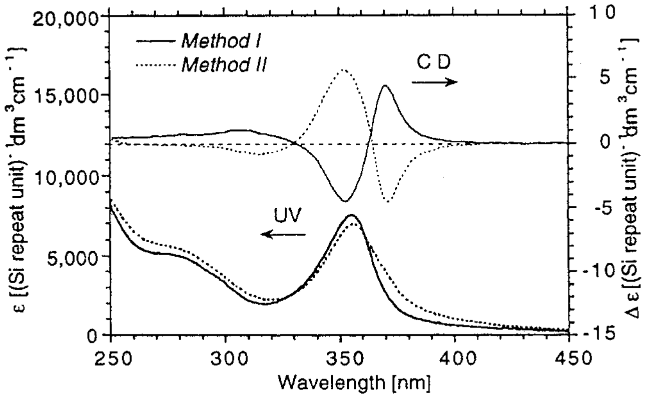


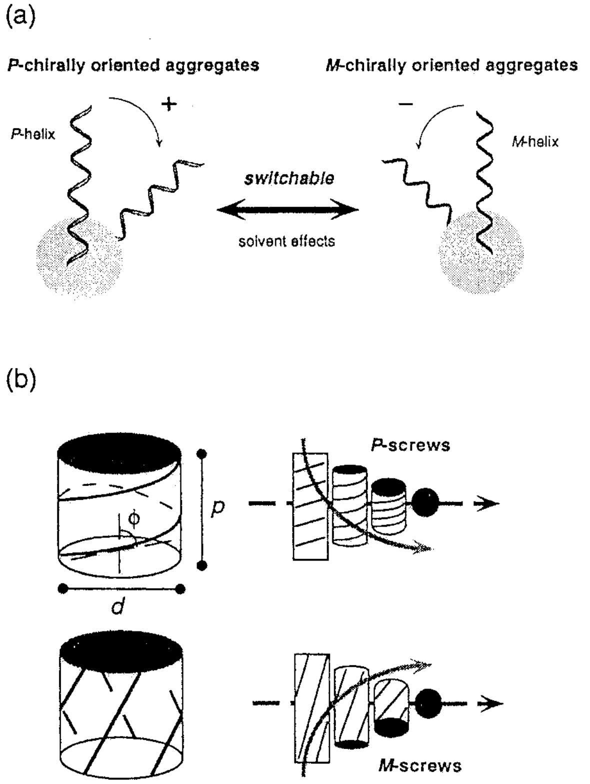
Figure 3. UV−vis and CD spectra of **1** aggregates prepared by Methods I and II at 55%/45% THF/methanol volume ratio at 20 °C.

Figure 2a,b shows the CD spectra and CD intensities of **1** aggregates prepared by the reverse solvent addition order method, Method II (THF solution of **1** added into methanol),[16] at various THF/methanol ratios at 20 °C, respectively. These bisignate CD spectra ($\lambda_{\mathrm{ext.}}$ around 370 and 353 nm) show similar signs and intensities to those prepared by Method I at the same THF/methanol ratios, though the band shapes between the two methods differ slightly, *except* at a THF/methanol ratio of 55%/45% (around the CD reversal point). At this point, samples prepared by the two methods exhibited completely mirror image Cotton effects, as shown in Figure 3, though no significant differences were evident in the UV spectra. This result indicates the formation of oppositely oriented chiral aggregates, controlled simply by the solvent addition order. This striking CD switching may be related to the dependence of the initially formed chiral "seed" aggregates on the solvent polarity,[18] since, comparing

---

[17] For example, if the *p*/*d* is smaller than π, right-handed screws generate a right-handed (*P*) superhelix; if the ratio is π, the screws are at 90° and their disposition is not chiral; if instead the ratio is greater than π, right-handed screws generate a left-handed (*M*) superhelix. See: Nakanishi, K.; Berova, N. In *Circular Dichroism: Principles and Applications*; Nakanishi, K., Berova, N., Woody, R. W., Eds.; VCH: New York, 1994; Chapters 5 and 13.

Scheme 2. Proposed Origin of the Cotton Effect of Polysilane Aggregates



Methods I and II, the only difference is the solvent polarity surrounding the seed aggregates in the initial stage of the aggregation process.Here, we suggest two possible origins of the CD switching phenomenon (relating to the oppositely oriented chiral seed aggregates) dependent on solvent polarity, though the detailed mechanisms are not clear at the moment: (1) The optical inactivity of **1** bearing a chiral group in a good solvent (due to the dynamic equilibrium between *P* and *M* screw sense turns)[11,12,15,19] may be essential for the switching phenomenon. We theoretically confirmed the existence of two equivalent potential energy dependencies on the backbone dihedral angle in both isotactic and syndiotactic models for **1** (H-(R$_1$R$_2$*Si)$_{30}$-H, where R$_1$ = *n*-hexyl and R$_2$* = *p*-(*S*)-2-methylbutoxyphenyl) by force field calculations (see Supporting Information). Presumably, the helical equilibrium in **1** may result in a preferential helical screw sense, *P* or *M*, upon aggregation by locking in the effects of the *p*-chiral ether moieties, while the solvent polarity may control the slight preference of **1** for *P*- or *M*-helicity. Consequently, the favorable chiral orientation (*P*- or *M*-superhelix) of **1** aggregates may be determined from the helicity of single molecule of **1** (Scheme 2a). (2) The helix angle ϕ governs the handedness of the packing between the preferential helical backbones of contiguous polysilane chains (there is no $P-M$ inversion of the helical single main chain) (Scheme 2b). In this model, the handedness of the superhelix depends on only two critical factors: the ratio of polymer helical screw pitch, *p*, to helical diameter, *d*, as has also been proposed for cholesteric liquid crystal phases of DNA.[17] Concerning polysilane aggregates in a good/poor cosolvent system, the screw pitch (*p*) of the preferential helicity could be largely dependent on the amount of poor solvent since the polysilane chains may shrink and fold (*p* becomes shorter) in excess poor solvent. It is thus considered that, also in this model, the solvent effects (solvation and solvent polarity) surrounding **1** in the aggregation process may hold the key to determine the handedness of the chiral superstructure.

We attempted the direct observation of the oppositely oriented chiral aggregate superstructures[20] using SEM and AFM; however, no evidence of the opposite chiral superstructures at the submicron level was obtained.

Thermal Effects on Chiroptical Properties of Polysilane Chiral Aggregates. To investigate the thermal CD dependency of **1** chiral aggregates, we subjected the aggregates to multiple cycles of heating (50 °C) and cooling (−10 °C). Figure 4a,b shows the change of CD intensities of **1** aggregates for both Methods I and II at 60%/40% and 50%/50% THF/methanol ratios in multiple thermal cycles, respectively. Interestingly, in the CD spectra of **1** aggregates at 60%/40% THF/methanol, the bisignate Cotton effect observed at 20 °C completely disappeared at 50 °C due to dissolution of the aggregates and appeared again at −10 °C on the cooling run (ca. 0.1 °C per s) (Figure 4a) with similar $\lambda_{\mathrm{ext.}}$ and sign to that at 20 °C, though the intensities were slightly weaker. These CD profiles were reproducible after several thermal cycles. In contrast, in the CD spectra at 50%/50% THF/methanol, we found an unprecedented thermo-driven CD switching phenomenon (Figure 4b). The CD bands at 353 and 323 nm of **1** aggregates for only Method II were reversed after four thermal cycles and the CD profiles finally showed similar CD $\lambda_{\mathrm{ext.}}$, signs, and intensities to those obtained by Method I (the band at 323 nm for Method II gradually appeared during thermal treatment). This CD switching for Method II appears to result from the transformation of a metastable chiral **1** aggregate to a stable opposite chiral state on application of the thermal stimulus. Presumably, in Method II, **1**, dropped into methanol (polar, poor solvent for **1**), may instantly form chiral oriented seed aggregates with intermolecularly folded and twisted Si main chains, even if energetically unfavorable (rapid coagulation process). The structure of this chiral aggregate may be thus metastable since it is affected sensitively by the medium of solvation. In contrast, in Method I, the chiral seed **1** aggregates grow slowly and moderately, and are therefore better able to adopt a stable structure (slow coagulation process). After thermal treatment, the metastable aggregates for Method II settle into the energetically more stable chiral configurations similar to that of Method I. It is thus suggested that the chirality of seed aggregates around 50%/50% THF/methanol may be easily controlled by the solvent addition order and that it is considerably sensitive to a thermal stimulus.

Solvent Effects on Chiroptical Properties of Polysilane Chiral Aggregates. The solvent polarity and solvation seem to be critical factors in the determination of the polysilane chiral aggregate structures. We therefore investigated the CD properties in another toluene (nonpolar, very good solvent for **1**)/

---

(18) Dielectric constant (ϵ) at 25 °C of solvents used in mixed solvent systems (unit: dimensionless number): THF, 7.58; methanol, 32.7; toluene, 2.38; acetonitrile, 35.9. These ϵ values were taken from the following: Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents Fourth Edition*; John Wiley & Sons: New York, 1986.

(19) (a) Meijere, A.; Khlebnikov, A. F.; Kostikov, R. R.; Kozhushkov, S. I.; Schreiner, P. R.; Wittkopp, A.; Yufit, D. S. *Angew. Chem., Int. Ed.* **1999**, *38*, 8, 3474. (b) Mislow, K.; Bickart, K. *Isr. J. Chem.* **1976/1977**, *15*, 1.

(20) (a) Ono, Y.; Nakashima, K.; Sano, M.; Hojo, J.; Shinkai, S. *Chem. Lett.* **1999**, 1119. (b) Cornelissen, J. J. L. M.; Fischer, M.; Sommerdijk, N. A. J. M.; Nolte, R. J. M. *Science* **1998**, *280*, 1427. (c) Frankel, D. A.; O'Brien, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10057. (d) Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. *Science* **1998**, *282*, 27. (e) Li, C. Y.; Cheng, S. Z. D.; Ge, J. J.; Bai, F.; Zhang, J. Z.; Mann, I. K.; Chien, L.-C.; Harris, F. W.; Lotz, B. *J. Am. Chem. Soc.* **2000**, *122*, 72. (f) Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 63.

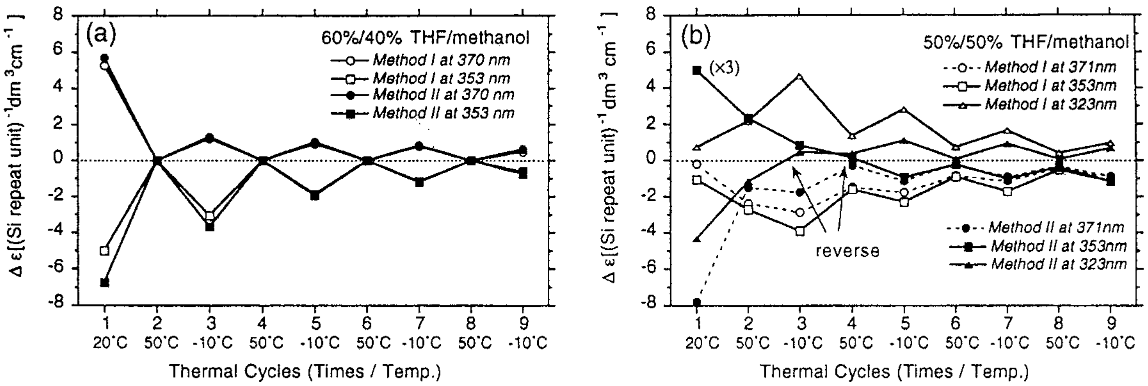


Figure 4. Change of CD intensity of **1** aggregates prepared by Methods I and II at (a) 60%/40% and (b) 55%/45% THF/methanol volume ratios in multiple thermal cycles of heating to 50 °C and cooling to −10 °C.

acetonitrile (highly polar, poor solvent for **1**) cosolvent system, whose dielectric constants are very different.[18] Figure 5a−c shows the CD spectra of **1** aggregates for both Methods I and II, and CD intensities at various toluene/acetonitrile ratios at 20 °C, respectively. The CD spectra in toluene/acetonitrile showed similar CD $\lambda_{\text{ext.}}$ around 370 and 350 nm and CD switching phenomena with the change of cosolvent ratios as for the THF/methanol system. However, there were two remarkable differences between the two cosolvent systems: (1) intense CD signals were observed even in excess toluene and (2) much white precipitation was found in the bottom of the cell, especially at a high acetonitrile ratio. These results suggest that in toluene/acetonitrile, **1** may aggregate easily due to the strongly polar acetonitrile. In contrast, in THF/methanol, **1** may have an affinity for methanol, regardless of its being a poor solvent, since poly(alkylalkoxyphenylsilane) has a polar oxygen in the side chain, therefore, the amount of precipitation for THF/methanol is less than that for toluene/acetonitrile.

Concerning the formation of stable chiral polysilane aggregates and the chirality switching, the orthogonal arrangement between the sterically crowded, polar *p*-alkoxy groups on the phenyl rings and the stiff main chain may be responsible for the unique CD properties. To test this, the chiroptical properties of two related **2** and **3** aggregates in toluene/acetonitrile were examined. Figures 6 and 7 show the CD spectra of **2** and **3** aggregates respectively for Method I at various toluene/acetonitrile ratios at 20 °C. Interestingly, although no Cotton bands of **2** and **3** aggregates were detected in THF/methanol (only a noisy peak), remarkable CD bands could be observed in toluene/acetonitrile, indicating the ease of formation of aggregates due to the effects of highly polar acetonitrile. As seen in Figure 6, for the less sterically hindered polar **2** which has a methyl group and a *p*-chiral alkoxy group on the phenyl ring, a weak, bisignate, nonswitchable CD signal (negative at $\lambda_{\text{ext.}}$ 365 nm, positive at $\lambda_{\text{ext.}}$ 345 nm) appeared, though no CD signals were evident in pure toluene or THF.[11] The CD intensities of **2** aggregates only gradually increased/decreased (Method I/II) on changing the toluene/acetonitrile ratio, and are different from the CD characteristics of **1** aggregates. However, it is clear that optically active chiral aggregates could also be induced in a different type of chirally substituted **2**.

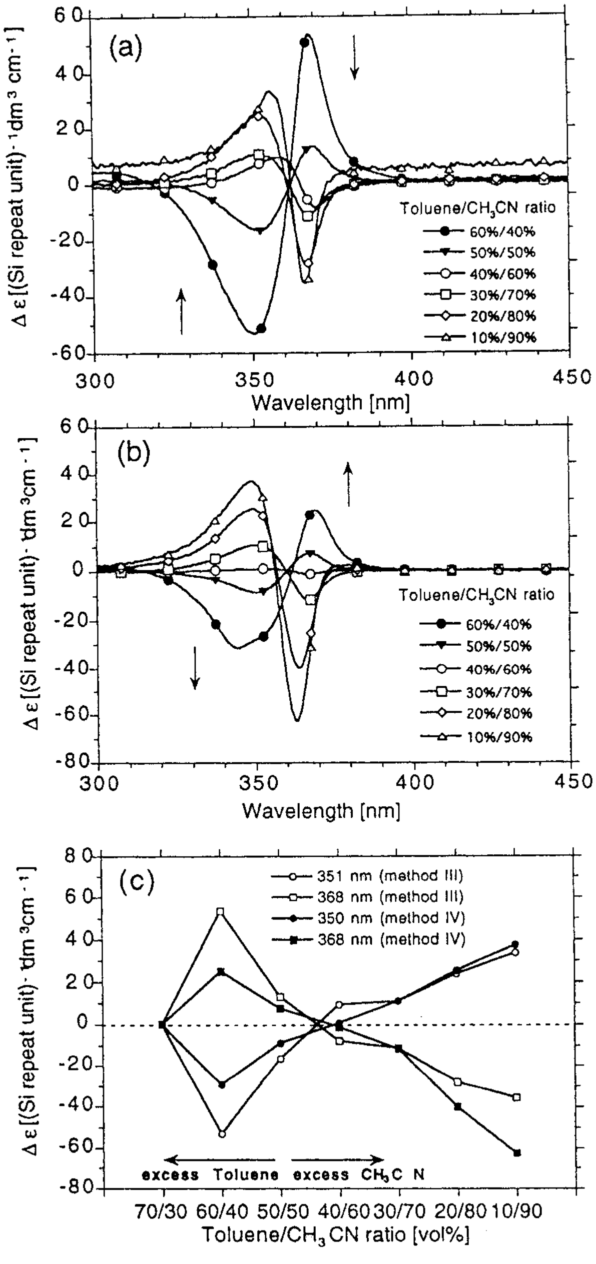


Figure 5. CD spectra of **1** aggregates prepared by Methods (a) I and (b) II and (c) a plot of CD intensities at various toluene/acetonitrile ratios at 20 °C.

No bisignate CD signals arising from aggregates could be detected for the even less sterically hindered, less polar **3**, however, which has a *m*-chiral alkoxy group on the phenyl ring (Figure 7), despite the observation of a negative CD signal at 310 nm when molecularly dispersed in pure THF or toluene.[11] Indeed, force field calculations for representative isotactic and syndiotactic models of **3** afforded asymmetric potential curves, indicating that the imbalance of energies of *P* and *M* screw senses should theoretically manifest itself in a preference for one screw sense over the other as observed for the experimental

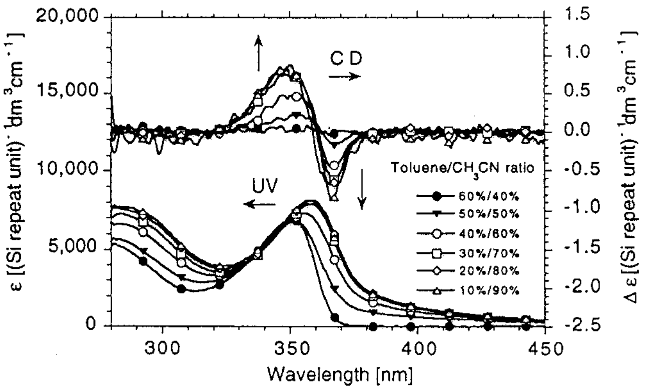


Figure 6. UV−vis and CD spectra of **2** aggregates prepared by Method I at various toluene/acetonitrile ratios at 20 °C.

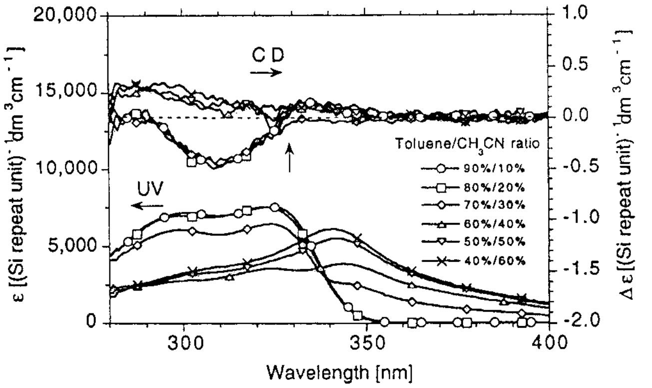


Figure 7. UV−vis and CD spectra of **3** aggregates prepared by Method I at various toluene/acetonitrile ratios at 20 °C.

molecularly disperse CD data (see Supporting Information). The UV spectra of **3** aggregates changed peculiarly with increasing acetonitrile and much white precipitate was observed above 30% acetonitrile. These results show that the optical activity of **3** in a good solvent solution disappeared in the aggregates in good/poor cosolvents, in contrast to the behavior for **1** or **2** chiral aggregates. Polysilane **3** originally has a preferential helical main chain and a slanting arrangement of the oxygen dipole to the Si main chain axis. The *meta*-position of the side chains sterically may obstruct the molecular packing of the chains, thereby inhibiting the formation of stable aggregates of preferential chirality.

Considering the difference of CD properties of **2** and **3** aggregates (**2**, no CD switching; **3**, CD disappearance) to those of **1** aggregates, the macroscopic conformations of polysilanes may also play an important role in the formation of stable aggregates and, when chiral substituents are attached, present the possibility of interesting CD switching phenomena. Polysilanes **2** and **3** have sterically imbalanced side chains, a small methyl group and a bulky (*S*)-2-methylbutoxyphenyl group, and may adopt conformations with macroscopically random and shrunk coils. In contrast, **1** with well-balanced *n*-hexyl and (*S*)-2-methylbutoxyphenyl groups adopts a stiffer coil. The extended Si main chain conformation and high spatial freedom between the bulky side chains may favor the formation of well-balanced, chirally oriented aggregates and permit chirality switching.

Consequently, it is clear that the formation of polysilane aggregates and the appearance of induced switchable CD properties in good/poor cosolvent systems involves various factors, including, for example, solvent polarity, solvation, solubility, solvent addition order, thermal effects, and polysilane structure and stereochemistry (side chain balance and the position of polar ether oxygen). We believe that such detailed experimental investigations of polysilane aggregates may help in the design of future generations of synthetic polymers with unique and functional chiroptical properties.

Conclusions

In summary, we succeeded in controlling the chiroptical characteristics of microaggregates of poly(alkyl-alkoxyphenylsilane)s by choice of good/poor solvent ratio (solvent polarity), solvent addition order, and temperature. It is clear that these CD properties result from chiral intermolecular interactions between helical polymers. The CD spectra of **1** aggregates with a dynamic equilibrium of *P* and *M* screw sense turns, were switched easily by selection of the good/poor solvent ratio and/or solvent addition order. In addition, the CD properties were also switchable thermally. The aggregates of less sterically hindered **2**, which has a *para* chiral alkoxy group on the phenyl ring, exhibited a weak, bisignate, nonswitchable CD signal in only the toluene/acetonitrile system, with no CD signals evident in pure toluene or THF due to masking of the helicity. In contrast, although the even less sterically hindered, less polar **3** which has a *meta* chiral alkoxy group showed optical activity when molecularly dispersed in pure THF or toluene, the CD signal disappears on formation of aggregates in good/poor cosolvent systems.

Experimental Section

Analysis. All UV and CD absorption spectra were recorded simultaneously on a JASCO J-725 spectrometer equipped with a Peltier controller for temperatures from 50 to −10 °C (1 cm path length quartz cell). Scanning conditions were as follows: a scanning rate of 50 nm per min, bandwidth of 1 nm, response time of 1 s, and double or single accumulations. 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 gel permeation chromatography on Shodex mixed gel KF80M as the GPC column and tetrahydrofuran 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. NMR spectra of the dichlorosilane monomers 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. 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.

Monomer Synthesis. The desired substituted dichlorosilane monomers were prepared by the condensation of the corresponding (*S*)-2-methylbutoxy-substituted phenyl Grignard reagent with the corresponding alkyltrichlorosilanes. Enantiopure chiral *para*- and *meta*-substituted (*S*)-2-methylbutoxyphenylbromides were custom synthesized by Chemical Soft Co., Kyoto, Japan. The monomer data are as follows. *n*-Hexyl-*p*-(*S*)-2-methylbutoxyphenyldichlorosilane (**5**): yield 49.0%; bp 140−145 °C/0.35 mmHg; ^{29}Si NMR 19.28 ppm; ^{13}C NMR 11.30, 14.05, 16.51, 20.01, 22.49, 22.54, 26.15, 31.33, 32.11, 34.69, 72.79, 114.61, 123.47, 135.14, 162.10 ppm; $[\alpha]^{22}_{D}$ +6.09° (neat). Methyl-*p*-(*S*)-2-methylbutoxyphenyldichlorosilane (**6**): yield 47.2%; bp 122−125 °C/1.0 mmHg; ^{29}Si NMR 18.64 ppm; ^{13}C NMR 5.71, 11.28, 16.49, 26.11, 34.65, 72.77, 114.61, 124.15, 134.82, 162.15 ppm; $[\alpha]^{24}_{D}$ +7.51° (neat). Methyl-*m*-(*S*)-2-methylbutoxyphenyldichlorosilane (**7**): yield 64.6%; bp 110−115 °C/0.8 mmHg; ^{29}Si NMR 18.20 ppm; ^{13}C NMR 7.04, 11.25, 16.79, 26.11, 34.73, 73.10, 110.65, 120.60, 133.73, 135.75, 163.50 ppm; $[\alpha]^{22}_{D}$ +6.23° (neat).

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 8.0 mL of dry toluene was added 0.50 g (2.3×10^{-2} mol) of sodium dispersion surface-activated by diglyme (10 μL) and 2.0 g (5.8×10^{-3} mol) of **5** dropwise under an argon atmosphere. The mixture was stirred slowly at 110 °C, monitoring the molecular weight periodically. After 1 h, 0.1 equiv of trimethylchlorosilane was added as terminator and stirring continued for a further 30 min. The viscous purple mixture was diluted with toluene and filtered through a 10 μm Teflon filter. The high molecular weight (M_w) fraction ($M_w = 1\,500\,000$; yield 12%) was isolated by centrifugation after fractional precipitation in a mixed 2-propanol−toluene solution and vacuum dried at 90 °C overnight. The yields and some properties of polysilanes **1**−**3** obtained in this work are summarized in Table 1. We also attempted to synthesize *m*-(*S*)-2-methylbutoxyphenyl-substituted polysilane with a long alkyl chain by a similar method: poly[*n*-hexyl-*m*-(*S*)-2-methylbutoxyphenylsilane] (**4**). High molecular weight polymers were not obtained, however, presumably due to high steric hindrance. (In this work, we also desired to investigate the molecular weight and polydispersity dependency of the observed chiral assembly phenomena; however, we could not extract purified low molecular weight components of polysilanes **1**−**3** by the toluene/alcohol separation method due to the high solubility of the products.)

Preparation of Polysilane Aggregates. Polysilane aggregates were prepared according to two methods. Method I: The polysilane was initially dissolved in a good solvent (THF or toluene; concentrated, 1×10^{-4} mol·L^{-1}). A poor solvent (methanol or acetonitrile) was then gradually added into the solution containing the polysilane with moderate stirring at room temperature. Method II: A good solvent solution containing the polysilane was gradually added into a poor solvent (the reverse solvent addition order method). After the samples prepared by both methods were stirred for 3 min, UV−vis/CD spectra were measured.

Molecular Mechanics Calculation. Molecular mechanics calculations were performed using the Molecular Simulation Inc., Discover 3 module, Ver. 4.00, on Silicon Graphics Indigo II XZ based on standard default parameters with a Si−Si bond length of 2.34 Å and a Si−Si−Si bond angle of 111° using the MSI pcff force field. For this calculation, the MSI built-in functions of simple-minimization and simple-dynamics were used with setup parameters which included 1.00 for the final convergency and a temperature of 300 K for the dynamics.

Acknowledgment. The authors would like to thank Drs. Hideaki Takayanagi, Masao Morita, and Keiichi Torimitsu for support. Dr. Akihiro Ohira is acknowledged for the molecular mechanics calculations. This work was supported by CREST (Core Research for Evolutional Science and Technology) of JST (Japan Science and Technology Corporation).

Supporting Information Available: Force field-calculated potential energy as a function of backbone dihedral angle for isotactic and syndiotactic models for **1** (H-(R_1R_2*Si)$_{30}$-H, where R_1 = *n*-hexyl and R_2* = *p*-(*S*)-2-methybutoxyphenyl), the representative isotactic and syndiotactic models for **3** (H-(R_1R_2*Si)$_{30}$-H, where R_1 = methyl and R_2* = *m*-(*S*)-2-methybutoxyphenyl) and UV and CD spectra of **2** and **3** aggregates at various toluene/acetonitrile ratios (Method II) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA000869H