

Chirality Control in Optically Active Polysilane Aggregates

Wenqing Peng, Masao Motonaga,[†] and Julian R. Koe*Contribution from the Department of Chemistry, International Christian University
(CREST-JST), Mitaka, Tokyo 181-8585, Japan

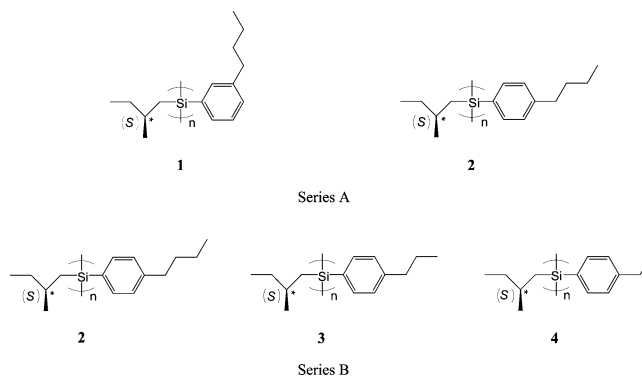
Received June 25, 2004; E-mail: koe@icu.ac.jp

Abstract: A novel strategy for controlling the higher order chirality of aggregates prepared from enantiopure polysilanes is experimentally probed and discussed. Structurally similar poly[*n*-alkyl(aryl)]silanes were synthesized in which one side chain comprised the chiral (*S*)-2-methylbutyl group and the other an achiral *m*- or *p*-alkyl-substituted phenyl ring. In solution the polymers adopt helical conformations with the same induced preferential screw sense chirality, as evidenced by circular dichroism (CD) spectroscopy. Aggregates, however, formed by addition of a nonsolvent to a polymer solution, show oppositely signed CD spectra. Consistent results were obtained for another series of poly[*p*-*n*-alkyl(aryl)]silanes where alkyl is butyl, propyl, and ethyl. The sense of the aggregate higher order chirality is dependent on the chemical composition and environment and is coarse-tunable by adjusting the length of the achiral side chain and fine-tunable by adjusting the good/poor solvent ratio. The origin of these effects is discussed with reference to a simple model.

Introduction

There is currently intense interest in the synthesis and control of chiral (helical) polymers.¹ Concerning the electronically σ -delocalized helical polysilanes, the great majority of these studies have reported the single molecule (i.e., solution state) characteristics.² However, any device-oriented application should be based on materials in the solid state, and as yet there are few reports concerning the control of polysilane chirality in the solid state, due to some extent to the problem of artifact signals which can arise, particularly in the CD spectra of film samples. One method to circumvent this is the study of the aggregate phase, in which intermolecular interactions occur, as in the solid state, but with the isotropic simplicity of the solution state. Using this approach, we reported our preliminary results concerning solvent effects on aggregate chirality (solvents type, addition order, polarity) in poly[alkyl(alkoxyphenyl)]silanes bearing a remote chiral group on the phenyl ring.³ However, the helicity control effects described in that paper may not survive through the process of making devices, since solvents will necessarily be removed. In this report, we would like to present a new strategy for controlling aggregate chirality by modification of the achiral side chain structure, which may be applicable also to other polymer systems, and in which solvent effects can be rendered ineffective or critical. The key advantages of this method are that aggregate chirality reversal does not require opposite enantiomer materials, can be rendered independent of solvent and single molecule screw sense, and depends only on the structure of the side chain.

Chart 1



Two series of poly[*n*-alkyl(aryl)]silanes are reported here, structurally similar to each other, in which the same enantiopure chiral (*S*)-2-methylbutyl group comprises one side chain (which has a conformational locking effect on the polymer helicity due to its proximity to the main chain)^{4,5} and a *m*- or *p*-*n*-butylphenyl group (**1** and **2**, respectively) or *p*-*n*-propylphenyl or *p*-ethylphenyl (**3** and **4**) comprises the other. Compounds **1** and **2** are discussed together as series A; **2**–**4** are discussed together as series B (see Chart 1).

Results and Discussion

Compounds **1**–**4** were obtained by the Wurtz coupling of the appropriate dichlorosilane monomers in toluene at 70 °C.⁶ Polymerization and spectroscopic data are given in Table 1.

[†] Current address: Tescom Co. Ltd., Tokyo 140-0015, Japan.

(1) (a) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1866. (b) Pu, L. *Macromol. Rapid Commun.* **2000**, *21*, 795–809. (c) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349–372. (d) Nolte, R. J. M. *Chem. Soc. Rev.* **1994**, *23*, 11–19.
(2) Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539–563.
(3) Nakashima, H.; Fujiki, M.; Koe, J. R.; Motonaga, M. *J. Am. Chem. Soc.* **2001**, *123*, 1963–1969.

(4) Fujiki, M.; Koe, J. R.; Terao, K.; Sato, T.; Teramoto, A.; Watanabe, J. *Polymer. J.* **2003**, *35*, 297–344.

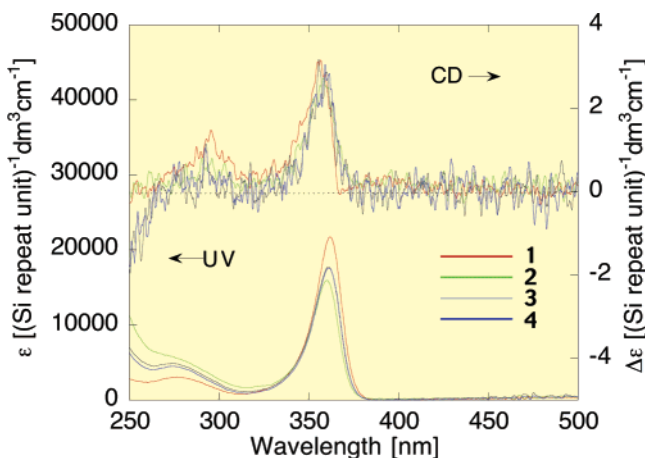
(5) (a) Koe, J. R.; Fujiki, M.; Nakashima, H. *Chem. Commun.* **2000**, 389–390. (b) Fujiki, M. *J. Am. Chem. Soc.* **2000**, *122*, 3336–3343. (c) Sato, T.; Terao, K.; Teramoto, A.; Fujiki, M. *Macromolecules* **2002**, *35*, 5355–5357.

(6) Hazard warning: proper precautions should be taken when handling both sodium and chlorosilanes. See also Supporting Information.

Table 1. Data for Polysilanes 1–4^a

	UV ^b	CD ^b	FL	$M_w^d/10^{-6}$	M_w/M_n	yield ^e /%	
	$\lambda_{\max}/\epsilon/\text{fwhm}$	$\lambda_{\max}/\Delta\epsilon$					$g_{\text{abs}}^c/10^4$
1	362/21600/18.2	357/3.20	1.48	378.6	2.66	2.41	1.3
2	360/15400/18.0	358/2.72	1.77	377.2	1.60	2.37	3.4
3	361/17500/18.0	359/2.82	1.61	377.9	5.88	2.36	10.1
4	361/17500/17.2	359/3.13	1.79	380.2	4.37	2.52	6.2

^a UV and fluorescence data in THF at 20 °C. ^b λ_{\max} units, nm; ϵ units, (Si repeat unit)⁻¹ dm³ cm⁻¹; fwhm = full width (nm) at half-maximum of λ_{\max} . ^c g_{abs} : ratio of CD and UV molar absorptivities. ^d Molecular weights determined by size exclusion chromatography (SEC) and relative to polystyrene standards; eluant, THF. ^e Isolated yields of high molecular weight fraction.

**Figure 1.** CD and UV spectra of polymers 1–4 in THF.

Solution-State Optical and Chiroptical Properties of Polysilanes. To discuss the structural dependence of the aggregate chirality clearly, it is helpful to first consider the solution-state characteristics. The polymers show relatively narrow (ca. 18 nm) UV absorptions due to the conjugated Si backbone $\sigma-\sigma^*$ transition, mirror image fluorescence emission spectra and small Stokes' shifts (ca. 16 nm), indicating regular semiflexible polymer molecules with a long segment length.⁷ The solution UV and CD spectra of 1–4 in tetrahydrofuran (THF) at 20 °C are shown in Figure 1.

All the polymers show positively signed Cotton effects in their solution CD spectra, coincident with the absorptions due to the Si $\sigma-\sigma^*$ transitions, which indicates that the backbones of 1–4 have the same prevailing helical screw sense in the solution state. The polymers have similar UV λ_{\max} , CD λ_{\max} , and dissymmetric ratio g_{abs} (defined as the ratio of CD and UV molar absorptivities). The similar UV λ_{\max} indicates that the polymers have similar Si main chain $\sigma-\sigma^*$ transition energies. These energies can be affected by steric and electronic effects of the side groups and the Si main chain segment length.⁷ Since groups in the para position can conjugate better with the silicon atom, electron donation from the *p*-*n*-butyl moiety in 2 may contribute more effectively to the σ -conjugating Si main chain through the phenyl ring than can the *m*-butyl moiety in 1.

The difference of donor effects in 1 and 2 is also supported by the ²⁹Si NMR chemical shifts: the resonance for 2 (–35.01 ppm) is shifted about 0.4 ppm upfield compared with that for 1 (–34.64 ppm), indicating that electron donation from the *p*-butyl moiety may occur more effectively and increase the electron density in the Si main chain. Such donation should

result in a longer wavelength UV λ_{\max} for 2. However, the UV λ_{\max} of polysilanes also depends on the global conformation of the Si main chain. The UV characteristics of polydialkylsilanes have been correlated with main chain extension and stiffness, revealing a bathochromic shift in the wavelength of the absorption maximum and an increase in molar absorptivity, ϵ , with a more rodlike nature.^{7,8} The UV molar absorptivity of 1 is about 1.4 times of that of 2, suggesting that 1 adopts a more extended main chain conformation than 2. Thus, the more extended main chain conformation of 1 appears to compensate for the less effective electron donation from the *m*-butyl moiety, resulting in a similar UV λ_{\max} to 2. The characteristics of 3 and 4, with *p*-propyl and *p*-ethyl substituents on the phenyl ring, respectively, are similar to those of 2, indicating similar conformations.

Aggregate State Chiroptical Properties of Polysilanes. Aggregates were formed by mixing a poor solvent (methanol or ethanol) with a solution of the polymers in a good solvent (THF or isooctane), as previously described.³ The aggregate UV absorptions occur at almost the same wavelength as in solution, but due to particle size-dependent light scattering by the aggregates, the intensities of the bands, though normalized to the same scale to account for concentration differences, are less consistent and tailing is observed on the long-wavelength side. The aggregate CD spectra are bisignate, which is considered to be characteristic of exciton coupling between closely situated transition dipole moments on neighboring polymer segments in chiral configurations.⁹ Although such effects may originate from either intramolecular¹⁰ or intermolecular³ interactions, a filtration experiment indicated that the size of the polymer aggregates was greater than 0.5 μm , showing that the interactions are largely intermolecular.

First, the results for polymers 1 and 2 (series A) will be discussed. The CD spectra of 1 and 2 aggregates are shown in Figure 2.

It is clear that the bisigned Cotton effects of 1 and 2 are opposite in nature, indicating aggregates of opposite chirality, despite the fact that they have the same positive CD signals in solution, as was evident in Figure 1, and thus also the same single molecule screw sense.

The opposite signs of the aggregate Cotton effects are not dependent on solvent polarity (no solvent-dependent switching is observed), solvent addition order, or good/poor solvent ratio, as the CD spectra of the aggregates show the same profile under conditions of normal or reverse order solvent addition and in different cosolvent systems (see Supporting Information). These results distinguish the present work from that reported in ref 3, in which solvent effects are critical. The key development in the present work is that the aggregate chirality can be controlled by structural modification in the achiral side chain, i.e., whether the *n*-butyl group is substituted para or meta on the phenyl ring.

We previously discussed a model of polysilane aggregate chirality³ with reference to the cholesteric hard core model,¹¹ in which the single molecule helical angle, ϕ , defined by the helical pitch, p , and diameter, d , governs the handedness of the

(8) Fujiki, M.; Toyoda, S.; Yuan, C. H.; Takigawa, H. *Chirality* **1998**, *10*, 667–675.

(9) Peeters, E.; Delmotte, A.; Janssen, R. A.; Meijer, E. W. *Adv. Mater.* **1997**, *9*, 493–496.

(10) Obata, K.; Kira, M. *Macromolecules* **1998**, *31*, 4666–4668.

(11) Nakanishi, K.; Berova, N. *Circular Dichroism: Principles and Applications*; Wiley-VCH: New York, 1994; Chapter 19.

(7) Fujiki, M. *J. Am. Chem. Soc.* **1994**, *116*, 11976–11981.

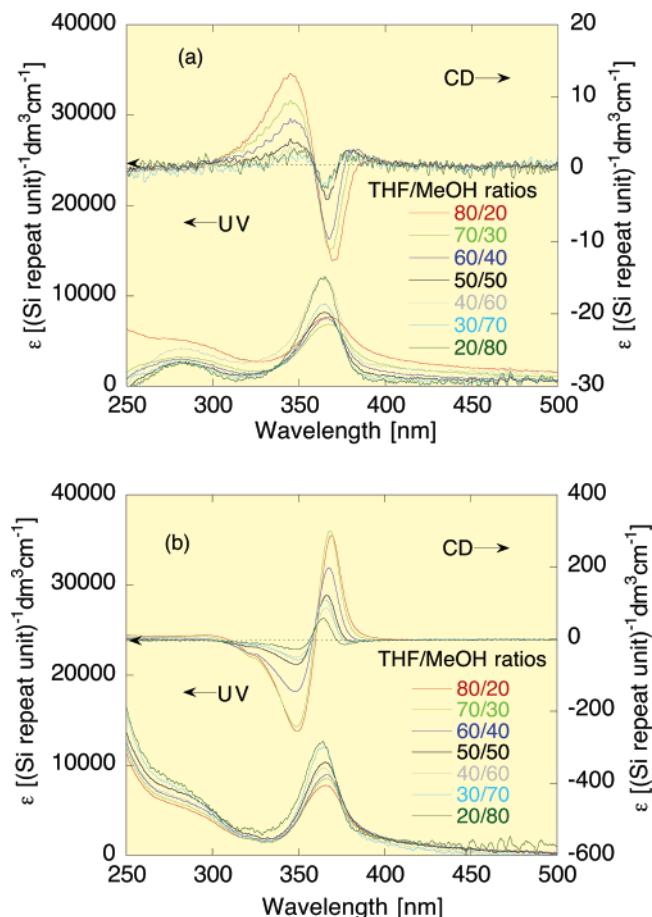


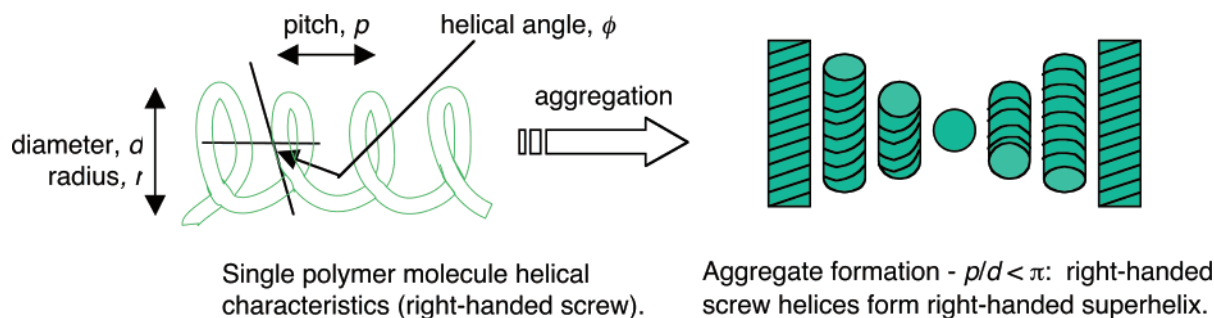
Figure 2. CD spectra of series A polymer aggregates (a) **1** and (b) **2**, prepared at various THF/MeOH ratios (20 °C).

packing between the preferential screw sense helical backbones of contiguous polysilane chains in aggregates (see Chart 2).

Based on this model, reversal of aggregate chirality can be achieved either by changing the single molecule screw sense or by changing the p/d ratio, since, for $p/d < \pi$, right-handed screws generate a right-handed (P) superhelix, whereas, for $p/d > \pi$, right-handed screws generate a left-handed (M) superhelix. It was shown above that **1** and **2** have the same preferential single molecule screw sense, so that, applying the model, their aggregate chirality should be dependent only on the p/d ratio. Although the p/d ratio may be susceptible to solvent effects during the formation of aggregates, as we suggested in our earlier paper,³ nonswitchable aggregate CD should be obtainable in a polymer if the value of the p/d ratio is sufficiently far from π . In that paper, solvent and temperature effects on the chiral aggregation of poly(alkylarylsilanes) bearing remote chiral

groups were reported, but it was difficult to clarify the key factor for controlling aggregate chirality because no preferential single molecule screw sense was observed in solution. The aggregate chirality switching by solvent effects in that report may result either from switching the preferential screw sense of single molecules, which is possible in polysilanes bearing a remote chiral group due to the greater conformational freedom,⁵ or from changing the p/d ratio. Concerning polymers **1** and **2** in this work, switching the single molecule screw sense is energetically unfavorable due to the strong backbone locking effect of directly attaching the (*S*)-2-methylbutyl moiety to the main chain,⁵ so it is thus possible to exclude single molecule screw sense switching effects as an origin of the aggregate chirality reversal. It is thus pertinent to consider the origins of variations in p and d for **1** and **2**. It is reasonable that the screw pitch, p , of the preferential helix depend on the backbone substituents of single polymer molecules, since more sterically demanding side chains result in a more extended main chain which should thus have a relatively longer screw pitch. It is thus considered that **1**, bearing an achiral *n*-butyl substituent in the meta-position of the phenyl ring, will adopt a more extended backbone conformation compared with **2**, which bears the same achiral substituent but in the para-position of the phenyl ring, due to the greater steric requirements of meta-substitution. In addition, **1** has a relatively smaller helical diameter than that of **2**, since with meta-substitution the maximum Si to side chain end distance is less than with para-substitution. Thus, if $p/d > \pi$ for **1** and $p/d < \pi$ for **2**, it is possible that opposite bisigned CD be obtained. However, more detailed comparison of **1** and **2** is difficult due to the fact that two variable parameters exist; i.e., both p and d differ in the polymers, and in particular, the variation of the helical pitch with side chain type is difficult to quantify. To circumvent these problems and confirm our hypothesis, we designed a second series of polymers, **2–4** (series B), in which only the length of the para-substituent in the aryl side chain varies, decreasing monotonically from **2** (*n*-butyl) to **4** (ethyl), with the intention to effect a chirality switch by reduction of d alone. The CD spectra of series B aggregates are shown in Figure 3. The CD spectra of all the series B aggregates are bisigned, with those of **4** clearly inverted relative to **2** (consistent with the discussion above of **1** and **2**), and those of **3** showing both positive and negative bisigned Cotton effects. The inverted spectra of **4** indicate opposite aggregate chirality to **2** aggregates, and since the single polymer molecules have the same preferential helical screw sense (the solution-state Cotton effects are both positive, as evident in Figure 1 above), the origin, according to the model, should arise in a decrease of the polymer chain diameter, d , resulting in a critical increase

Chart 2. Aggregate Chirality Dependent on Single Polymer Molecule Helical Characteristics (Adapted with Permission from Ref 3)



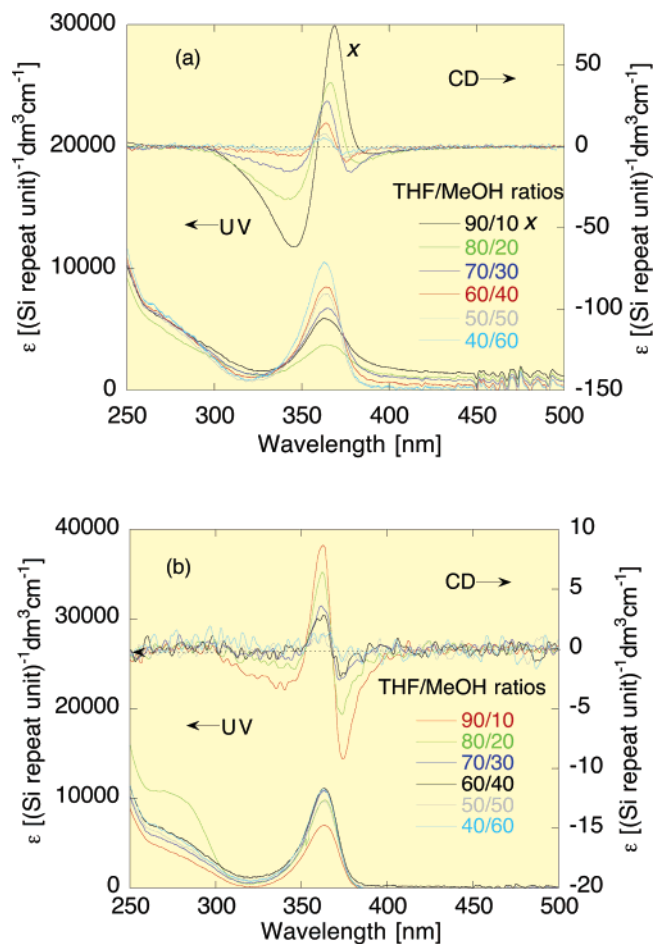


Figure 3. UV and CD spectra of series B polymer aggregates (a) **3** and (b) **4**, prepared at various THF/ethanol ratios (20 °C). The intensity of the curve marked “x” in (a) is scaled down by a factor of 2.

of the p/d ratio to greater than π and a concomitant aggregate chirality inversion. It thus appears that control of the polymer diameter alone may be sufficient to effect a chirality inversion in the aggregate phase. The CD spectra of **3** indicate a similar chiral aggregate configuration at low ratios of poor to good solvent (positive bisigned CD), but an inverted aggregate chiral configuration at high ratios of poor to good solvent. It is considered that, for this polymer, the structural “coarse tuning” results in a p/d close to π and that the aggregate chirality can then be “fine tuned” by solvent effects. These results support the considerations above even better than anticipated, since the aggregate chirality can be controlled not only by selection of the achiral phenyl substituent chain length but also by solvent under certain conditions.

Calculations of Helical Parameters. The experimental results above are further supported by simple calculations (see Table 2).¹² The parameters of the helix may be considered as follows: diameter, d , is the internal diameter of a cylinder into which the polymer would just fit and is evaluated by doubling, r_{tot} , the sum of the silicon core radius, r_{Si} ($=0.685$ Å), and the distance from a silicon atom to the end of its longer side chain (alkylphenyl, p -R-Ph; extended chain), r_{SC} ; pitch, p , may be evaluated as the distance between two silicon atoms after one full helical turn and depends on the backbone dihedral angle,

Table 2. Data from Calculations on 16-mer Models of Series B Polymers

polymer	R	$r_{\text{SC}}/\text{Å}$	$r_{\text{Si}}/\text{Å}$	$r_{\text{tot}}/\text{Å}$	$d/\text{Å}$	θ/deg	$p/\text{Å}$	p/d
2	<i>n</i> -Bu	10.25	0.685	10.935	21.87	165	61.48	2.81
3	<i>n</i> -Pr	8.94	0.685	9.625	19.25	165	61.48	3.19
4	Et	7.92	0.685	8.605	17.21	165	61.48	3.57

θ , which, for a model 16-mer, was set at 165° . The backbone dihedral angle was set at 165° since this is the value obtained previously for a structurally similar model (isotactic poly[*n*-hexyl((*S*)-2-methylbutoxyphenyl)silane]) using force field calculations.^{4,13} It is also reasonable that the backbone dihedral angle is the same in all the series B polymers, since they show the same UV λ_{max} . It should be recognized that the accuracy of calculations involving polymers is very much lower than that of small molecules and that the data here should be taken only as showing what is reasonable and possible.

Using the values obtained for d and (with θ set at 165°) a value of 61.48 Å for p , the values of p/d fit the model and experimental data remarkably well. For **2**, with $p/d < \pi$, a particular handedness of screw sense in a single molecule should afford aggregates with the same handedness of superhelix, while for **4**, with $p/d < \pi$, the same particular handedness of screw sense in a single molecule should afford aggregates with the opposite handedness of superhelix. Further, the value of p/d obtained for **3** is very close to π , and it is as expected that the intermediate chain length of the *n*-propyl group as compared with the *n*-butyl and ethyl affords an intermediate value of p/d . It is then reasonable that solvent effects may be sufficient to slightly alter p/d , resulting in the observed solvent-induced aggregate chirality switching.

It is thus evident that, depending on the actual values of p and d , the ratio of p/d could be greater than π , less than π , or very close to π in the series B (and also series A) polymers, depending on the nature of the side chain. By careful choice of substituents, the chirality of aggregated polymer phases can be simply controlled: with p/d sufficiently far from π , aggregates with opposing, stable chirality can be formed (structural coarse tuning), and with p/d near π , aggregates with solvent-switchable chirality can be formed (solvent fine-tuning). These concepts may be applicable in the understanding and development of solid-state chirality, not only in the polysilanes but also in other polymers.

In summary, we have demonstrated the first examples of polysilane aggregates, the chirality of which was simply controlled by the position or length of the achiral group at the phenyl ring (coarse tuning) and is not dependent on single molecule screw sense reversal. Depending on the substituents selected, solvent effects can be rendered critical, such that the aggregate chirality can be fine-tuned by the solvent nature or composition. Further investigations directed toward the control of polymer chirality are in progress.

Experimental Section

See Supporting Information.

Acknowledgment. The authors would like to thank Prof. Michiya Fujiki of Nara Institute of Science and Technology for fruitful discussions and CREST-JST for funding. The Japan

(12) Calculations were performed using CS Chem3D Pro v. 5.0 with standard bond lengths.

(13) Nakashima, H. Ph.D. Thesis, Waseda University, Tokyo, 2002, Chapter 4, p 85.

Society for the Promotion of Science is also acknowledged for research funding and a postdoctoral fellowship for W.P.

Supporting Information Available: Experimental details, including aggregate CD spectra of **1** and **2** in isooctane/ethanol, monomer data comprising boiling points, optical rotation, yields,

^1H , ^{13}C , and ^{29}Si NMR data, and polymer data comprising NMR data for **1**–**4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA046235I