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Transfer and Amplification of Chiral Molecular Information to Polysilylene Aggregates

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Chiral molecular information exercises a great influence on our physiological action, and the recognition and assignment of chirality between two mirror-image enantiomers are thus vital subjects, especially for the pharmaceutical industry. A few synthetic helical polymers are known to act as chiral selectors,[1] and are in wide use as the chiral stationary phase (CSP) in gas or liquid chromatography.[2] For chiral selection, highly polar side pendants on the polymers, capable of multiple and strong interactions between the guest enantiomers and host polymer through, for example, hydrogen bonding, dipole−dipole, ionic, or acid−base interactions, are indispensable. Here we demonstrate the chirality recognition of chiral alcohols using aggregates[3] of achiral, chromophoric poly(*n*-hexyl-*p*-*n*-propoxyphenylsilylene) **1** (Chart 1), a polymer molecule which bears only relatively weakly polar ether groups. This is a simple method for chiral detection and is applicable for weak interactions between chiral guests and host polymers, since the chiral molecular information is transferred to the polymer and then amplified by the formation of polymer aggregates. Complexes of **1** aggregates with chiral alcohols exhibit remarkable, bisignate-induced circular dichroism (ICD) based on amplified chiral ordering. Additionally, the sign of the ICD depends on the absolute configuration of the chiral alcohol, indicating a potential as a high-throughput screening probe for the chirality assignment of chiral guests.

Figure 1 shows the CD and UV spectra of **1** aggregates in a mixture of toluene/(*S*)- or (*R*)-2-butanol (**2**)/methanol (poor solvent for **1**) at 20 °C. Achiral **1** naturally shows no CD signals in either molecularly dispersed solution or as aggregates. However, when mixed with (*S*)- or (*R*)-**2** a marked chirality-dependent bisignate ICD signal was exhibited. In the UV spectra, no significant differences were evident. These results indicate clearly that **1** formed chiral-oriented aggregates due to the transfer of chiral information from an external chiral source. We recently reported a similar example of induced optical activity in aggregates in good/poor cosolvents for poly(*n*-hexyl-*p*-(*S*)-2-methylbutoxyphenylsilylene), which itself bears enantiopure chiral pendants, although the polymer is optically inactive in molecularly dispersed solution.[4] The bisignate ICD effects in the chiral aggregates may originate via exiton coupling between neighboring polymer chains in chiral superstructures,[5] such as occurs in the packing of cholesteric liquid crystals. The induction of chirality in **1** aggregates may be essential for the transfer of chiral information by weak hydrogen-bonding interaction between the ether oxygen moieties of **1** and the OH group of **2**.[6] In addition, the orthogonal arrangement between the polar *p*-alkoxy groups and the stiff main chain of **1** may be critical for effective chirality transfer. Indeed, the complexes of related poly(*n*-hexyl-*p*-*n*-butylphenylsilylene) (no ether oxygen) aggregates with **2** exhibited no ICD peaks, and *m*-substituted, poly(*n*-hexyl-*m*-*n*-propoxyphenylsilylene) aggregates revealed ICD intensities about one-third that of *p*-substituted **1** aggregates.

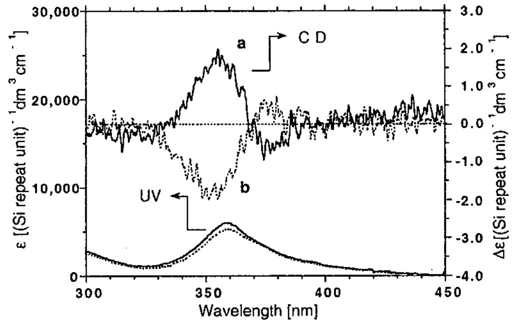
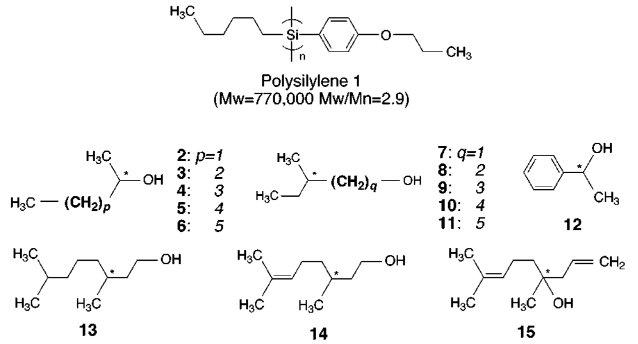


Figure 1. CD and UV spectra of **1** aggregates in toluene/(*S*)-**2** (a; solid line) or (*R*)-**2** (b; dotted line)/methanol mixtures at 20 °C.

Chart 1. Structures of Polysilylene **1** and Chiral Alcohols (**2**−**15**)



The complex of **1** aggregates with chiral phenylethanol (**12**) showed an intense ICD (see Table 1 and Supporting Information), indicating that **12** could be bound strongly with the side chain of **1** through both hydrogen bonding and phenyl $\pi-\pi$ interactions. However, poly(*n*-hexyl-*p*-*n*-butylphenylsilylene) aggregates with **12** exhibited no ICD, indicating that phenyl $\pi-\pi$ interaction alone is not sufficiently strong.

The **1** chiral aggregates showed a linear relation between the enantiomeric excess (ee) of **2** and the ICD intensities (see Supporting Information), in contrast to helical polyisocyanate,[1a,7]

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(3) Polysilylene aggregates were prepared as follows; **1** was initially dissolved in toluene (concentrated 5×10^{-4} mol·L^{-1}). Chiral alcohols and successively methanol were gradually added into the **1**−toluene solution with moderate stirring at room temperature. After stirring for 1 min, UV/CD spectra were measured. The volume ratio of all toluene/chiral alcohol/methanol mixtures was 30/50/20 vol %.

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(6) Interestingly, the chirality transfer could not be observed in the mixture of only **1**−toluene−chiral guests (without methanol) or when the chiral guests were added after formation of the aggregates. This implies that the phenomenon may require a definite order of the *transfer* (binding between chiral guests and polysilylene) and then *amplification* (formation of the aggregates as involving chiral guests in the hosts).

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Table 1. Signs of Bisignate Cotton Effects and Molar Circular Dichroic Absorption (Δε) for **1** Aggregates[a]

chiral cmpd		first Cotton		second Cotton	
		sign	$\Delta\epsilon$ (λ_{max})[b]	sign	$\Delta\epsilon$ (λ_{max})[b]
2	(*S*)-(+)	−	0.59 (376.6)	+	1.76 (354.8)
	(*R*)-(−)	+	0.55 (376.6)	−	1.87 (354.0)
3	(*S*)-(+)		*c*	+	0.11 (354.8)
	(*R*)-(−)		*c*	−	0.11 (355.0)
4	(*S*)-(+)	−	2.58 (369.2)	+	2.31 (351.9)
5	(*S*)-(+)	−	0.95 (369.5)	+	1.33 (351.9)
6	(*S*)-(+)	−	0.63 (371.7)	+	1.12 (353.2)
	(*R*)-(−)	+	0.80 (371.3)	−	1.06 (353.1)
7	(*S*)-(−)	+	0.17 (373.8)	−	0.51 (355.2)
8	(*S*)-(+)	−	0.70 (373.3)	+	0.85 (354.0)
9	(*S*)-(+)	+	0.40 (379.0)	−	0.28 (353.1)
10	(*S*)-(+)	−	0.38 (375.0)	+	0.26 (355.0)
11	(*S*)-(+)	+	0.34 (377.0)	−	0.49 (357.0)
12	(*S*)-(−)	−	6.12 (371.0)	+	7.86 (351.5)
	(*R*)-(+)	+	5.82 (371.3)	−	5.71 (351.1)
13	(*S*)-(−)	−	1.38 (372.5)	+	1.33 (350.1)
	(*R*)-(+)	+	1.27 (371.7)	−	2.06 (351.5)
14	(*S*)-(−)	−	1.67 (371.3)	+	1.66 (354.8)
	(*R*)-(+)	+	1.07 (371.3)	−	1.24 (353.2)
15	(*R*)-(−)		*d*		*d*

[a] All CD data were recorded on a Jasco J-725 spectropolarimeter in toluene/chiral alcohol/methanol (=30/50/20 (vol %)) mixtures at 20 °C. [b] Δε units: (Si repeat unit)$^{-1}$dm^{-3}cm^{-1} and λ_{max} units: nm. [c] The exact Δε value could not be estimated because of noisy peaks. [d] No CD peaks could be observed.

polyacetylene[1d] and polythiophene aggregates, [8a] which have been shown to exhibit nonlinear ee responses. The latter nonlinear effect is due to the cooperative behavior of the chiral side chains or chiral guests bound to polymer and is known as the "majority rules" concept. The reason that **1** aggregates do not display a "majority rules" effect is presumably a consequence of the weaker interaction between the chiral guests and the host polymer: The advance of this, though, is that the present system can determine the optical purity of chiral targets quantitatively.

For chiral guests, we focused on a series of (*S*)-chiral secondary (**2**−**6**) or primary (**7**−**11**) alkyl alcohols with different numbers of methylene groups (Chart 1), and systematically investigated the ICD properties of **1** aggregates with these chiral alcohols. The results of the ICD studies are summarized in Table 1. Figure 2a,b illustrates the ICD intensities and signs at the second Cotton effect of **1** aggregates. Interestingly, the ICD sign of **1** aggregates with (*S*)-primary alcohols (**7**−**11**, Figure 2b) oscillated according to the number of methylene carbons (*q*) from the OH group to the chiral center. Additionally, the absolute magnitude was also sensitive to *q*. These results indicate a clear odd−even effect in the CD properties. A similar odd−even alternation effect has been observed in chiroptical measurements using plane-polarized light or CD on certain helical superstructures such as some cholesteric liquid crystalline compounds, helical poly(isocyanides) with mesogenic substituents,[9] and helical polythiophene aggregates in solution.[8b] From exiton theory and model studies, it is empirically suggested that the odd−even effect originates in the transition between right (*P*)- and left (*M*)-handed supermolecular helicity.

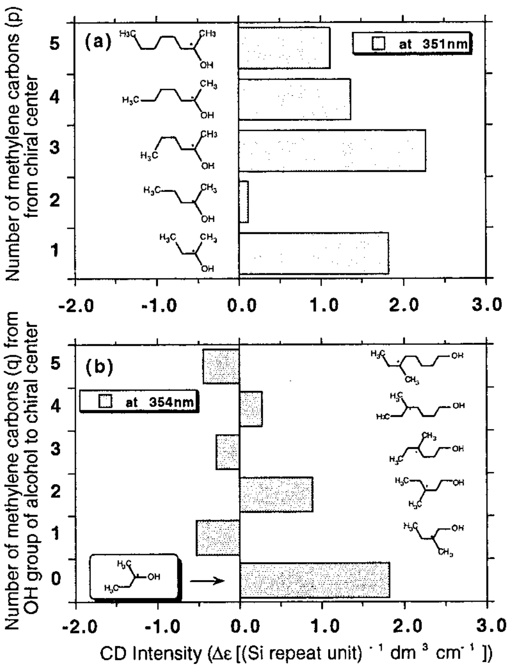

Figure 2. Plot of CD intensities of **1** aggregates in toluene/series of (*S*)-chiral alkyl alcohols (a; secondary (**2**−**6**), b; primary (**7**−**11**))/methanol mixtures at 20 °C. (For comparison, the ICD intensity with (*S*)-**2** is inserted in (b), *q* = 0).

It is therefore possible that a *P*−*M* transition of helically ordered **1** aggregates might also occur, dependent on the distance from the OH group to the chiral center of the primary chiral alcohol, although the detailed mechanism is not clear at the moment. (ICD spectra with related **13** and **14** containing a branched methyl group in the terminal position exhibited features similar to those of **8**). In contrast, in the ICD spectra of **1** aggregates with (*S*)-secondary alkyl alcohols (**2**−**6**; in Figure 2a only the (*S*)-absolute configuration is plotted), the ICD sign showed only a positive second Cotton effect and was independent of the number of methylene carbons (*p*). These results also mean that the position of the chiral center might govern the chirality of **1** aggregates, since the chiral center in the secondary alcohols is always in the α position, even though *p* is different. The tertiary chiral alcohol (**15**) gave no CD peaks, indicating that the bulkiness of **15** presumably hinders interaction with **1**.

In this work, the host polysilylene aggregates exhibited a highly responsive and characteristic ICD, depending on the stereochemistry of the guest chiral alcohols. We believe that this is applicable for other synthetic, choromophoric polymers, and that the preparation of a library by screening against various chiral guests (by combinatorial techniques) might assist in the design of new polymer-based CSPs or chiral sensors.

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Supporting Information Available: Monomer and polymer data, figures exhibiting the linear effect between the ICD intensities of **1** aggregates at 354 nm and the % ee of **2**, the CD and UV spectra with **12**, examples of the odd−even effects observed in the ICD spectra with **7** and **8**, and estimated particle sizes of **1** aggregates with **2** or **12** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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