Supporting Online Material for

Chiroptical generation and inversion during the mirror-symmetry-breaking aggregation of dialkylpolysilanes due to limonene chirality

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This article is part of the ChemComm 'Chirality' web themed issue

Experimental Section

Instrumentation

The CD and UV spectra of the solution were recorded simultaneously at 25 °C on a JASCO J-820 spectropolarimeter equipped with a Peltier-controlled housing to control the stir speed, direction and temperature. An SQ-grade quartz cuvette was used with path lengths of 5 mm and 10 mm, a scanning speed of 100 nm min⁻¹, a bandwidth of 1 nm, a response time of 1 s and single accumulation. The CPL and PL spectra were recorded at 25 °C on a JASCO CPL-200 spectrofluoropolarimeter without a Peltier-controlled housing and with an SQ-grade quartz cuvette. A path length of 10 mm, a scanning rate of 100 nm min⁻¹, an excitation bandwidth of 10 nm, a monitoring bandwidth of 10 nm, a response time of 2 s and single accumulation were employed. To obtain a high S/N ratio, the angle between the incident and travelling light was adjusted to 0° using a notch filter. The optical rotation at the Na-d line was measured with a JASCO P-1020 polarimeter using a path length of 10 mm at room temperature. Chiral gas chromatography (Shimadzu GC-2010), using a Supelco β -DEX-120 with 30 m \times 0.25 mm ID, was used to determine the enantiopurity of the limonenes. A column oven temperature program was used to set an initial temperature of 40 °C, a heating rate of 20 °C min⁻¹ and then hold at 85 °C for 20 min; He at a flow rate of 1.2 mL min⁻¹ served as the carrier gas. The weight-average molecular weight (M_w) , number-average molecular weight (M_n) and polydispersity index $(PDI = M_w/M_n)$ were evaluated by gel permeation chromatography (GPC) at 40 °C on a Shimadzu A10 instrument with a PLgel (Varian) 10-um mixed-B column. HPLC-grade THF was used as the eluent and the measurements were calibrated using polystyrene standards (Varian).

Chiroptical analysis

The magnitude of circular polarisation in the ground state is defined as $g_{CD} = 2 \times (\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$, where ε_L and ε_R denote the extinction coefficients for left and right circularly polarised light, respectively. The magnitude of circular polarisation in the excited state is defined as $g_{CPL} = 2 \times (I_L - I_R)/(I_L + I_R)$, where I_L and I_R indicate the output signals for left and right circularly polarised light, respectively. Experimentally, the value of g_{CD} is defined as $\Delta \varepsilon/\varepsilon = [\text{ellipticity}/32,980] / \text{absorbance at the CD extremum, and the value of <math>g_{CPL}$ is defined as $\Delta I/I = [\text{ellipticity}/(32,980/\ln 10)] / \text{unpolarised PL intensity at the CPL extremum.}$

Materials

Spectroscopic grade THF and methanol (Dotite) were used to prepare the polymer solutions for measurements. (*R*)-Limonene and (*S*)-limonene were obtained from Wako (Tokyo, Japan) and purified by reduced pressure prior to use. (*R*)-limonene: $[a]^{27}_{589} = +101.55^{\circ}$ (neat), > 99.1 % *ee*; (*S*)-limonene: $[a]^{27}_{589} = -103.19^{\circ}$ (neat), > 99.3 % *ee*. To obtain the data shown in Fig. 2a, we used (*R*)-limonene and (*S*)-limonene as received.

A series of poly(dialkylsilane)s (**PSi1-PSi4**) was produced according to a previously described synthetic approach. The CD and UV spectra of (R)-limonene and (S)-limonene in n-hexane at 25 °C indicate that their signals do not interfere with the chiroptical CD and UV spectra of PSis or their aggregates between 225 and 800 nm, even in the chiral tersolvent system.

Preparation of optically active PSi aggregates

A typical procedure for the production of PSi aggregates in a mixed THF/limonene/ methanol solvent is described below. First, limonene was added to 0.3 mL of THF stock solution containing PSi (5.0×10^{-4} mol L⁻¹ of the Si repeating unit) in a 10 mm path length cuvette (or 0.15 mL in a 5 mm path length cuvette) which was placed in the Peltier apparatus and stirred clockwise for 10 sec at 800 rpm at 25 °C. Methanol was then added at 25 °C, resulting in a white turbid solution of PSi aggregates dispersed in the solvent. After stirring for 30 sec, this solution was immediately used for CD/UV and CPL/PL spectroscopic measurements. The total amount of solvent was 3.0 mL in a 10 mm path length cuvette and 1.5 mL in a 5 mm path length cuvette, respectively. The final concentration of the Si repeating unit was 5.0×10^{-5} mol L⁻¹.

We characterized the aggregate size by a series of membrane filters with several pore sizes, although the dynamic light scattering (DLS) technique might provide information of the size and its distribution of the aggregates. We applied a DLS technique to evaluate $\sim \mu$ m-order aggregates, but failed due to out of range of the instrument (upto 1 μ m; Otsuka DLS-6000, Japan). The aggregate size was determined to be $\sim 5 \mu$ m by membrane filter experiments [Y. Nakano and M. Fujiki, *Macromolecules*, 2011, **44**, 7511–7519].

Synthesis and Characterisation of PSis



Scheme S1. Synthesis of PSi1, PSi2 and PSi3.

Synthesis of *n*-decyl-isobutyldichlorosilane (1)

Magnesium turning (7.3 g, 0.3 mol) and THF (100 mL) were placed in a three-necked flask under N₂ and the surface of the Mg was activated by adding a few drops of 1,2-dibromoethane. To this solution, *n*-C₁₀H₂₁Br (Aldrich, 55.3 g, 0.25 mol) was added dropwise for 30 min and the mixture was kept at 50 °C for 30 min. A solution of *n*-decylmagnesium bromide was obtained. To a mixture of isobutyltrichlorosilane (Shin-Etsu, 47.9 g, 0.25 mol) and THF (50 mL) at 50 °C held in another three-necked flask, *n*-decylmagnesium bromide solution was added dropwise for 1 h and was kept at 50 °C for 2 h. The monomer was purified by distillation in a vacuum (bp 134 °C/ 4.2 mmHg). Yield: 38.6 g (52.0 %). ¹³C NMR (125 MHz, CDCl₃) 32.5, 31.9, 30.4, 29.6, 29.4, 29.3, 29.1, 25.6, 24.2, 22.7, 22.4, 21.3, 14.1; ²⁹Si NMR (100 MHz, CDCl₃) 33.7.

Synthesis of poly(*n*-decyl-isobutylsilane) (PSi1)

To a mixture of dry toluene (Wako, 40 mL), sodium (Kanto, 3.07 g, 133 mmol) and 18-crown-6 (Wako, 167 mg, 0.631 mmol), dichlorosilane **1** (10 g, 33.6 mmol) was added dropwise under an N₂ atmosphere. The mixture was slowly stirred at 120 °C for 2 h. An additional 500 mL of dry toluene was added to reduce the solution viscosity and stirring was continued for another 30 min. The hot-reaction slurry was passed immediately through a $2-\mu m$ PTFE filter (Fluoropore F-40 and Fp-200, Sumitomo Electric) under an N₂ gas atmosphere. To the clear filtrate, ethanol and methanol were carefully added. Several fractions of the white precipitate were collected by centrifugation (Kubota 5420, 3000 rpm) and dried overnight at 120 °C in a vacuum. ²⁹Si NMR (100 MHz, CDCl₃) –23.3.

Synthesis of *n*-decyl-2-ethylbutyldichlorosilane (2)

Magnesium turning (7.3 g, 0.3 mol) and THF (100 mL) were placed in a three-necked flask under N₂ and the surface of the Mg was activated by adding a few drops of 1,2-dibromoethane. To this solution, 2-ethylbutylbromide (Aldrich, 41.3 g, 0.25 mol) was added dropwise for 30 min and the mixture was kept at 50 °C for 30 min. A solution of 2-ethylbutylmagnesium bromide was obtained. To the mixture of *n*-decyltrichlorosilane (Shin-Etsu, 68.9 g, 0.25 mol) and THF (50 mL) held at 50 °C in another three-necked flask, *n*-decylmagnesium bromide solution was added dropwise for 1 h. The final mixture was kept at 50 °C for 2 h. The monomer was purified by distillation in a vacuum (140 °C/ 2.7 mmHg). Yield: 32.7 g (40.0 %). ¹³C NMR (125 MHz, CDCl₃) 35.9, 32.5, 31.9, 29.6, 29.5, 29.4, 29.2, 27.7, 24.8, 22.7, 22.5, 21.3, 14.1, 10.5; ²⁹Si NMR (100 MHz, CDCl₃) 33.6.

Synthesis of poly(*n*-decyl-2-ethylbutylsilane) (PSi2)

To a mixture of dry toluene (Wako, 40 mL), sodium (Kanto, 3.07 g, 133 mmol) and 18-crown-6 (Wako, 167 mg, 0.631 mmol), dichlorosilane **2** (10 g, 30.8 mmol) was added dropwise under an N₂ atmosphere. The mixture was slowly stirred at 120 °C for 2 h. An additional 500 mL of dry toluene was added and stirring was continued for another 30 min. The hot-reaction slurry was passed immediately through a $2-\mu$ m PTFE filter (Fluoropore F-40 and Fp-200, Sumitomo Electric) under an N₂ gas atmosphere. To the clear filtrate, ethanol and methanol were carefully added. Several fractions of the white precipitate were collected by centrifugation (Kubota 5420, 3000 rpm) and dried overnight at 120 °C in a vacuum. ²⁹Si NMR (100 MHz, CDCl₃) –20.6.

Synthesis of *n*-decyl-*rac*-2-methylbutyldichlorosilane (3)

Magnesium turning (7.29 g, 0.3 mol) and THF (50 mL) were placed in a three-necked flask under N₂ and the surface of the Mg was activated by adding a few drops of 1,2-dibromoethane. To this solution, *rac*-2-methylbutylchloride (TCI, 26.7 g, 0.25 mol) was added dropwise over a period 30 min. The reaction mixture was kept at 50 °C for 30 min. A solution of *n*-decylmagnesium bromide was obtained. To the mixture of *n*-decyltrichlorosilane (Shin-Etsu, 68.9 g, 0.25 mol) and THF (50 mL) held at 50 °C in another three-necked flask, *n*-decylmagnesium bromide solution was added dropwise over a period of 1 h. The final mixture was kept at 50 °C for another 2 h. The moiety was purified by being distilled in vacuum (139 °C/3.3 mmHg) Yield: 33.4 g (43.0 %). ¹³C NMR (125 MHz, CDCl3) 32.5, 32.3, 31.9, 30.2, 29.6, 29.4, 29.3, 29.1, 28.0, 22.6, 22.4, 21.8, 21.3, 14.0, 11.1; ²⁹Si NMR (100 MHz, CDCl₃) 33.0.

Synthesis of poly(*n*-decyl-*rac*-2-methylbutylsilane) (PSi3)

To a mixture of dry toluene (40 ml), sodium (3.07 g, 0.133 mol) and 18-crown-6 (167 mg, 0.631 mmol), monomer **3** (10 g, 32.2 mmol) was added dropwise under an N₂ atmosphere. The mixture was slowly stirred at 120 °C. After 2 h, 500 mL of dry toluene was added to reduce the solution viscosity and stirred for another 30 min. The hot-reaction slurry was passed immediately through a 2- μ m PTFE filter (Fluoropore F-40 and Fp-200, Sumitomo Electric) under an N₂ gas atmosphere. To the clear filtrate, ethanol and/or methanol were carefully added. Several fractions of the white precipitate were collected by centrifugation and dried overnight at 90 °C in a vacuum. ²⁹Si NMR (100 MHz, CDCl₃) –22.0.

Synthesis of *n*-decyl-(*S*)-2-methylbutyldichlorosilane (4*S*) and poly(*n*-decyl-(*S*)-2-methylbutyldichlorosilane) (PSi4*S*)

The synthesis procedures followed to produce compound **4***S* and **PSi4***S* were compiled into a Japanese patent. **4***S*, bp 120 °C/ 0.4 mmHg ¹³C NMR (125 MHz, CDCl₃) 32.5, 32.4 31.9, 30.2, 29.6, 29.5, 29.3, 29.2, 28.1, 22.7, 22.5, 21.8, 21.3, 14.1, 11.2; ²⁹Si NMR (100 MHz, CDCl₃) 33.2. [M. Fujiki, Jpn. Tokkyo Kokai JP H06-306087 (1994) along with related publications. M. Fujiki, *J. Am. Chem. Soc.*, 1994, **116**, 6017–6018; M. Fujiki, *J. Am. Chem. Soc.*, 1996, **118**, 7424–7425; K. Okoshi, H. Kamee, G. Suzaki, M. Tokita, M. Fujiki and J. Watanabe, *Macromolecules*, 2002, **35**, 4556–4559].

Supporting Data

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Fraction no	$M_{ m w}/10^5$	${M}_{ m n}/10^{5}$	$M_{ m w}/M_{ m n}$
F1	3.34	1.90	1.75
F2	2.15	0.94	2.28
F3	0.50	0.33	1.51
F4	0.27	0.21	1.26
F5	0.19	0.15	1.25

Table S2. Molecular weight and molecular-weight distribution of PSi2.

Fraction no	$M_{ m w}/10^5$	${M}_{ m n}/10^{5}$	$M_{ m w}/M_{ m n}$
F1	1.37	1.01	1.35
F2	0.64	0.52	1.21
F3	0.35	0.29	1.21
F4	0.11	0.09	1.24

Table S3. Molecular weight and molecular-weight distribution of PSi3.

Fraction no	$M_{ m w} / 10^5$	${M}_{ m n}/10^{5}$	$M_{ m w}/M_{ m n}$
F1	16.30	6.06	2.69
F2	10.20	4.42	2.31
F3	4.22	2.64	1.60
F4	2.50	1.62	1.54
F5	1.64	1.17	1.40
F6	1.54	1.09	1.41
F7	1.02	0.72	1.41
F8	0.54	0.46	1.18
F9	0.23	0.20	1.15



Figure S1. CD and UV spectra of various molecular weights of (*a* and *b*) **PSi1**, (*c* and *d*) **PSi2** and (*e* and *f*) **PSi3** in a chiral tersolvent at 25 °C under the following optimised volume fraction of THF/limonene/methanol: (*a* and *b*) 0.30/0.30/2.40 (v/v/v), (*c* and *d*) 0.30/1.50/1.20 (v/v/v), (*e* and *f*) 0.30/1.10 /1.60 (v/v/v), [Si repeating unit] = 5.0×10^{-5} mol L⁻¹, with a path length of 10 mm.



Figure S2. The limonene/methanol ratio dependent UV and CD spectra of (*a* and *b*) **PSi1** (M_w = 7.8 × 10⁴), (*c* and *d*) **PSi2** ($M_w = 13.7 \times 10^4$), (*e* and *f*) **PSi3** ($M_w = 10.2 \times 10^4$) and (*g* and *h*) **PSi4** ($M_w = 14.4 \times 10^4$) in a chiral tersolvent, [Si repeating unit] = 5.0 × 10⁻⁵ mol L⁻¹, with a path length of (*a*–*f*) 10 mm, (*g*, *h*) 5 mm. THF/(limonene + methanol): (*a*–*f*) 0.30/2.70 (v/v), (*g*, *h*) 0.15/1.35 (v/v).

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Figure S3. (Left) Potential energy surface of *n*-hexyl-(*S*)-2-methylbutylsilane 31-mer (**PSi5S**) with *it*- and *st*-sequences as a function of main-chain dihedral angle calculated by MSI Discover 3 (Ver. 4.00) with pcff force field (Si–Si bond length of 2.34 Å and Si–Si–Si bond angle of 111°). (Right) Configurational model of *it*- and *st*-sequences.