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# Cooperative C–F···Si interaction in optically active helical polysilanes†

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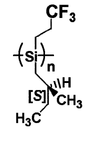
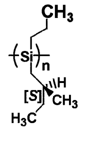
**Cooperative amplification of the C–F···Si weak interaction between side chains and the main chain was found to afford rigid rodlike helical polysilanes with a preferential screw sense.**

Well-ordered secondary and tertiary structures in naturally occurring macromolecules (*e.g.* proteins and genes) are the consequence of a subtle balance among various noncovalent interactions.[1] In polymer science, such noncovalent interactions have been utilized in well-designed synthetic polymers, especially helical polymers, leading to an intended change in their conformation and physical properties.[2] Up to now, the interactions employed for such purposes have been relatively strong ones, such as acid-base complexes,[3] hydrogen bonding[4] and metal coordination.[5] However, even tiny interactions, if induced into polymers, may be amplified with cooperativity and eventually could affect the global conformation of polymers.[6] Conversely, such phenomena might be applied in order to probe a very weak interaction which may be hard to detect when separately existing in small molecules.

We synthesized fluoroalkyl-containing chiral polysilanes, **PS-1**, **PS-3** and **PS-5** using the conventional Wurtz-type coupling reaction in boiling *n*-nonane.[7,8] For comparison, analogous dialkyl chiral polysilanes, **PS-2**, **PS-4** and **PS-6** were also prepared.


**PS-1**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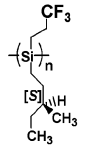
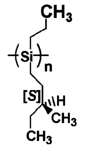
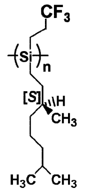
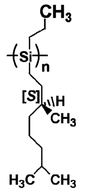

**PS-3**


**PS-4**


**PS-5**


**PS-6**

The optical properties of polysilanes strongly depend on the conformation of their chromophoric backbone composed entirely of σ-conjugated Si–Si bonds.[9] Especially, their helical sense can be characterized by the Kuhn dissymmetry ratio ($g_{\mathrm{abs}} = \Delta\varepsilon/\varepsilon$).[10,11] Fig. 1 shows the UV, circular dichroism (CD) and fluoroscence (FL) spectra of **PS-1** and **PS-2** in THF at 20 °C. The value of molar absorptivity ($\varepsilon$) of **PS-1** is 9 000 (Si-repeat-unit)$^{-1}$ dm$^3$ cm$^{-1}$ at 309.6 nm, while that of **PS-2** is 15 800 (Si-repeat-unit)$^{-1}$ dm$^3$ cm$^{-1}$ at 314.0 nm. Except for the slightly blue shifted absorption peak ($\lambda_{\max}$) of **PS-1** relative to that of **PS-2**, the other parameters from the spectra of **PS-1** and **PS-2**, that is, $g_{\mathrm{abs}}$ ($\Delta\varepsilon/\varepsilon$), fwhm (full width at half maxium) and Stokes' shift, are almost the same, which means that the helical conformation of polysilanes with the chiral β-branched alkyl substituent is not significantly affected by the replacement of the *n*-propyl group with a 3,3,3-trifluoropropyl group. However, this replacement brings about a considerable variation in the helical conformation of polysilanes with the chiral γ-branched alkyl substituent as shown in Fig. 2. The UV and CD spectra of **PS-3** showed typical characteristics of a stable helical chain having a preferential screw-sense, with $\varepsilon$ of 17 600 (Si-repeat-unit)$^{-1}$ dm$^3$ cm$^{-1}$ at 318.0 nm, $g_{\mathrm{abs}}$ of 1.09 × 10$^{-4}$ and fwhm of 13.6 nm in THF at 20 °C, while those of **PS-4** exhibited a very weak Cotton effect and broad UV absorption in spite of the same chiral side chain. For **PS-3**, the FL spectral profile is the mirror image of the absorption band with a Stokes' shift of 9.8 nm. However, for **PS-4**, the FL spectral profile with fwhm of 21.8 nm is not the mirror image of the relatively broad absorption band. Consequently, the mirror image relationship shows that **PS-3** has a more regular spatial conformation than **PS-4**. Fluorine substitutions of hydrogen normally do not significantly perturb the structure of a polymer because fluorine and hydrogen have similar van der Waals radii.[12] This helical bias for single screw-sense in **PS-3** can be explained with the chain stiffness induced by the intramolecular weak interaction between the pendant neutral F atoms and the Si

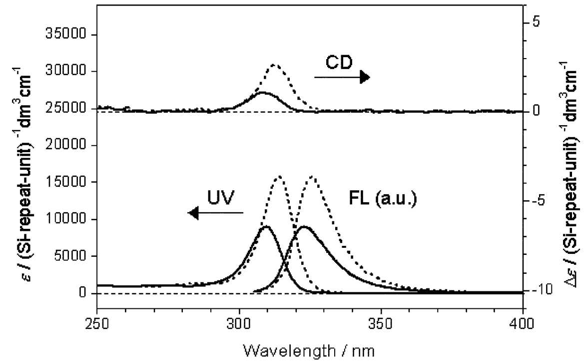


**Fig. 1** UV, CD and FL spectra of **PS-1** (solid line) and **PS-2** (dashed line) in THF at 20 °C; **PS-1**: $M_{\mathrm{w}}$ = 5 000, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.27, Conc. = 7.77 × 10$^{-5}$ M, **PS-2**: $M_{\mathrm{w}}$ = 4 500, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.16, Conc. = 8.00 × 10$^{-5}$ M.

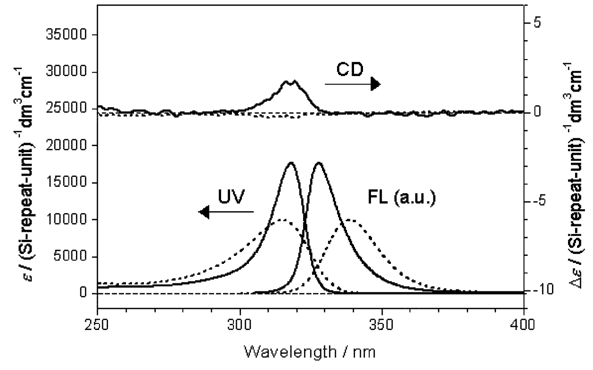


**Fig. 2** UV, CD and FL spectra of **PS-3** (solid line) and **PS-4** (dashed line) in THF at 20 °C; **PS-3**: $M_{\mathrm{w}}$ = 17 000, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.84, Conc. = 6.61 × 10$^{-5}$ M, **PS-4**: $M_{\mathrm{w}}$ = 79 000, $M_{\mathrm{w}}/M_{\mathrm{n}}$ = 1.65, Conc. = 8.82 × 10$^{-5}$ M.

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† Electronic Supplementary Information (ESI) available: experimental section, $^{29}$Si NMR of **PS-5** and **PS-6**, variable-temperature $^{29}$Si NMR of **PS-5** and **PS-6**, $^{19}$F NMR of **PS-1** and **PS-5**, and IR spectra of **PS-5**. See http://www.rsc.org/suppdata/cc/b3/b314723a/

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backbone.[13] In fact, all polysilanes having chiral side-chains do not adopt a stable helical conformation and chain rigidity to some degree is prerequisite.[10] The absence of the effect of C–F···Si interaction in **PS-1** may be due to either its low molecular weight which cannot show cooperativity or the β-branched alkyl substituent which can prevent the interaction with steric hindrance.

The existence of a marked C–F···Si weak interaction can be also found in another high molecular weight polysilane, **PS-5** with a chiral γ-branched alkyl substituent. Fig. 3 shows the temperature dependence of $\varepsilon$ and $\Delta\varepsilon$ for **PS-5** and **PS-6**. In the case of **PS-6**, the UV absorption and Cotton effect are weak in the range of temperature from −40 to 80 °C. However, the UV absorption and Cotton effect for **PS-5** are fairly strong compared to those for **PS-6** and strongly depend on the solution temperature. This distinct temperature dependence for **PS-5** indicates that the C–F···Si weak interaction is dynamic in solution. The population of F atoms which effectively interact with the Si backbone decreases with increasing temperature to give a semi-rigid chain.

The main-chain rigidity induced by the C–F···Si weak interaction can be also supported by $^{29}$Si NMR in $CDCl_3$ at 30 °C; $\Delta\nu_{1/2} = 76.8$ Hz at −25.1 ppm for **PS-5** and $\Delta\nu_{1/2} = 26.4$ Hz at −24.6 ppm for **PS-6**. The remarkable difference in $^{29}$Si NMR signal linewidth ($\Delta\nu_{1/2}$) is related closely to the degree of main-chain rigidity and mobility of the polysilanes.[14] The greater degree of rigidity of **PS-5** compared to **PS-6** is suggested by the broader $\Delta\nu_{1/2}$. The upfield chemical shift for **PS-5** relative to that for **PS-6**, in spite of the electron withdrawing effect of F atoms, might result from the intramolecular interaction between the pendant F atoms as neutral donors and the Si backbone with d orbitals of appropriate energy. On the other hand, the chemical shifts of Si for **PS-1** and **PS-2** are identical (−22.6 ppm), which implies that the C–F···Si interaction in **PS-1** is insignificant and is consistent with the results of optical measurements. The dynamic behavior of the C–F···Si weak interaction in solution was also investigated by variable-temperature $^{29}$Si NMR measurements in toluene-$d_8$.[15] The linewidth of **PS-5** gradually reduced from 83.2 to 44.8 Hz as the temperature increased from r.t. to 80 °C, while that of **PS-6** was almost temperature-independent. Although the chemical shifts of both **PS-5** and **PS-6** shifted downfield with increasing temperature, the signal of **PS-5** changed more sensitively to temperature than that of **PS-6** and eventually two peaks had the same chemical shift at 80 °C.

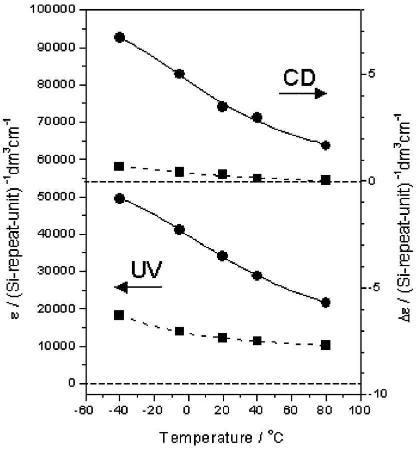

**Fig. 3** CD ($\Delta\varepsilon$, at $\lambda_{ext}$) and UV ($\varepsilon$, at $\lambda_{max}$) molar absorptivities of **PS-5** and **PS-6** in isooctane as a function of temperature; **PS-5** (circles, solid line): $M_w = 330\,000$, $M_w/M_n = 3.06$, Conc. $= 2.80 \times 10^{-5}$ M, **PS-6** (squares, dashed line): $M_w = 1\,700\,000$, $M_w/M_n = 1.79$, Conc. $= 7.43 \times 10^{-5}$ M.

The intramolecular C–F···Si weak interaction can influence the C–F stretching vibration. The IR absorption spectrum of **PS-5** showed the splitting of C–F bands having almost the same intensity at 1213 and 1198 cm$^{-1}$. The higher and lower frequencies could be assigned to free C–F and C–F interacting with the Si backbone, respectively, because intramolecular interactions, including hydrogen bonding, usually shift the absorption band to lower frequency.[4] Meanwhile the lower frequency band became very weak in the IR spectrum of **PS-1**, which indicates the interaction is negligible as mentioned above.

Although the $^{19}$F NMR peaks of **PS-1** and **PS-5** were not clearly assignable because they may contain information of tacticity, they gave an indication of the mobility of the fluoroalkyl groups. In the case of **PS-1**, there were only broad peaks, which means that the fluoroalkyl groups in **PS-1** were frozen through tight packing with 2-methylbutyl groups. However, the $^{19}$F NMR spectrum of **PS-5** showed additional narrow peaks at 69.9 and 70.1 ppm. These peaks can be assigned to F dynamically interacting with Si by means of NOE difference spectra and variable-temperature $^{19}$F NMR measurements.

In summary, we synthesized the first optically active polysilanes containing a fluoroalkyl moiety. The intramolecular cooperative C–F···Si weak interaction affects the rigidity of the polysilanes, leading to their stable helical conformation. The β-branches in **PS-1** may prevent the interaction with steric hindrance, while the γ-branches in **PS-3** and **PS-5**, which are located at the same radial distance as the F atom from the Si backbone, can facilitate the interaction.

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