A New Screw-Sense Switchable Polysilylene with Quantized and Superposed Helicities

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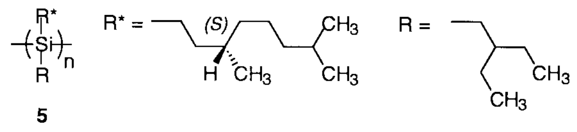
A new rod-like polysilylene bearing a *β*-branched alkyl group, poly[(*S*)-3,7-dimethyloctyl(2-ethylbutyl)silylene], was found to undergo a thermo-driven, helix–helix transition at –7 °C in isooctane associated with the discontinuous changes in the singlet σ–σ* excitation energy in the silicon backbone in the switching temperature region.

Designing and synthesizing bi- and multi-stable switching photonic materials able to reversibly respond to external biases are now challenges in molecular[1] and polymer[2] material sciences. Chromotropic polysilylenes[3,4] may be candidates for such materials due to changes in the main chain transition energy and the intensity characteristic of the one-dimensional exciton absorption bands in the near-UV region. Recently, certain rod-like dialkylpolysilylenes bearing two *γ*-branched alkyl side chains on each silicon atom were found to undergo helix–helix transitions in isooctane upon application of a thermal energy bias: poly[(*S*)-3,7-dimethyloctyl(3-methylbutyl)silylene] (**1**) and poly[(*R*)-3,7-dimethyloctyl((*S*)-3-methylpentyl)silylene] (**2**) have transition temperatures (T_c) of –20 and 2 °C, respectively.[5] However, rod-like polysilylenes with *β*-branched chains, poly[(*S*)-3,7-dimethyloctyl(2-methylpropyl)silylene] (**3**) and poly[decyl((*S*)-2-methylbutyl)silylene] (**4**), did not exhibit any such transition.[6]



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We now report that a specific, new rod-like polysilylene bearing a *β*-branched alkyl group, poly[(*S*)-3,7-dimethyloctyl-(2-ethylbutyl)silylene] (**5**, M_w=14500, M_n=11300, M_w/M_n = 1.28)[7] undergoes an exceptional helix-helix transition at –7 °C in isooctane, associated with the discontinuous changes in the lowest σ–σ* excitation energy (E_{max}) in the silicon backbone near 3.8 eV in the switching temperature region.

As shown in Figure 1, the lowest positive-signed CD band at 3.76 eV of **5** in isooctane at 25 °C is almost the inverse of the negative-signed CD band at 3.80 eV at –18 °C, indicating that a preferential screw-sense can effectively switch between the two temperatures. Although these Cotton bands might be ascribed to an almost 7_3-helical structure with the *P*- or *M*-screw-sense of dialkylpolysilylenes,[8] the helical motifs at –18 and 25 °C are energetically nonequivalent. Noted that both **5** and **3** have the same *γ*-branched chiral and a similar *β*-branched achiral chain, a choice of the achiral moiety thus definitively determines the capability of the preferential screw-sense inversion.

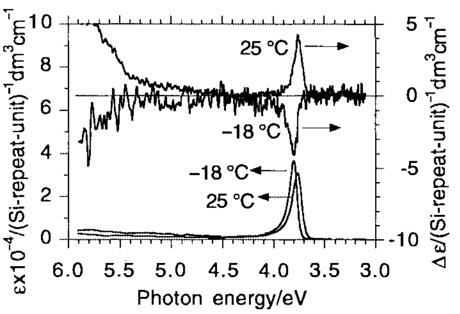

Figure 1. CD and UV absorption spectra of **5** in isooctane at –18 and 25 °C.

Figure 2 shows the variable temperature CD ($\Delta\varepsilon$) and near-UV (ε) band intensities of **5** near 3.8 eV in isooctane between 80 and –82 °C. The value of $\Delta\varepsilon$ slightly increases from 3.5 at 80 °C to 4.2 at 25 °C, but goes to zero at the T_c of –7 °C, and then inverts to –8.5 at –82 °C, while the value of ε monotonically increases from 27000 at 80 °C to 47000 at –82 °C. Although these high ε values are characteristic of rod-like polysilylenes, the increase in the ε value may be rationalized with the progressive increase in the radius of gyration of the polysilylene in solution.[6]

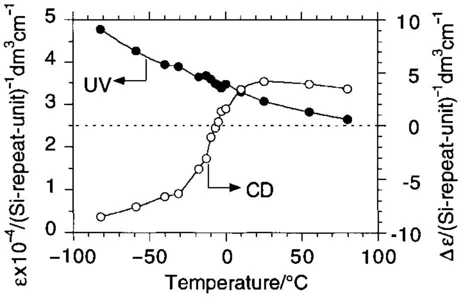

Figure 2. CD ($\Delta\varepsilon$, open circles) and UV (ε, filled circles) band intensities of **5** around 3.8 eV in isooctane in the range 80 to –82 °C.

To quantitatively evaluate the *PM*-population of **5** in solution, one may use the dimensionless parameter, the dissymmetry ratio, g_{abs} (defined as $\Delta\varepsilon/\varepsilon$), of **5** at each temperature by reference to the regression curve of the $g_{\rm abs}$ values for **3** assumed to be in a purely *P*-motif.[5] This conformation analysis was previously applied to those of **1** and **2**.[5,6] The *PM*-population of **5** in isooctane as a function of temperature is plotted in Figure 3.

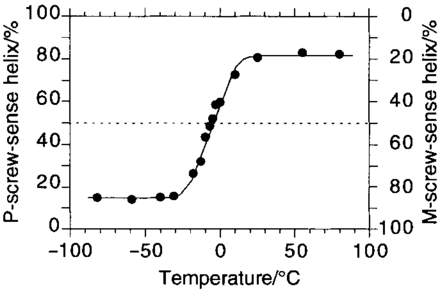

Figure 3. Population of *P*- and *M*-motifs in **5** in isooctane as a function of temperature, evaluated using the $g_{\rm abs}$ values of **5** by reference to the regression curve of the $g_{\rm abs}$ values for **3**.[5]

It is evident that **5** features three thermally accessible regions, A (–80 to –30 °C), B (–30 to 25 °C), and C (25 to 80 °C), as already demonstrated in **2**. In region A, **5** contains a constant 15% *P* and 85% *M* (70% *M*-excess), but on the other hand, in region C, it has an 82% *P* and 18% *M* (64% *P*-excess). The switching features in region B are thus ascribed to be the consequence of the quantized and superposed helicities between the 70% *M*- and 64% *P*-excess states, although the superpositions of chirality and optical activity were classically discussed by Hund, and later by several quantum physicists.[9]

With respect to the polysilylene helicities,[5] cooperativity in the coupled conformational and electronic transitions has been theoretically discussed for polyenes,[10] and this has already been theoretically and experimentally established for the stiff helical polyisocyanates.[11] Therefore, it is expected that evidence of a significant structural change of the backbone and side chains in **5** may be spectroscopically observable.

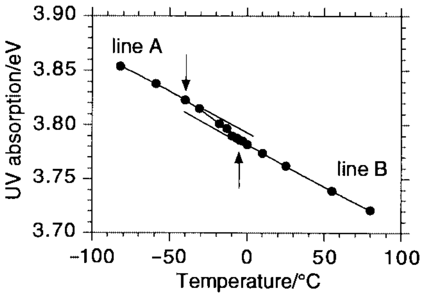

Figure 4. Temperature dependent $E_{\rm max}$ values of **5** in isooctane.

The temperature dependent $E_{\rm max}$ values of **5** in isooctane are shown in Figure 4. Although a progressive shift of $E_{\rm max}$ to the higher energy is seen with decreasing temperature, two discontinuous changes around –40 and –10 °C are recognized. By extrapolating the two straight lines A and B, the energy gap is estimated to be ~ 0.01 eV, implicating the occurrence of slight conformational changes in the Si–Si main chain structure to relax the overcrowded steric environment of the three methyl groups at the δ-position of the chiral and achiral side chains.

This idea may be connected to noticeable differences in the ^{29}Si NMR chemical shift between **5** and **3** in $CDCl_3$: $\Delta\nu_{1/2}$ = 70 Hz at –17.5 ppm for **5** at 40 °C, and $\Delta\nu_{1/2}$ = 65 Hz at –22.7 ppm for **3** at 20 °C.[4] Although the stiffness of **5** is almost similar to that of **3**, the significant downfield shift of ~ 5 ppm for **5** implies an elongation of the Si–Si bonds due to the steric demand.[5,6]

In conclusion, we have demonstrated that a polysilylene bearing a β-branched alkyl group **5** undergoes a helix–helix transition at –7 °C in isooctane, associated with the discontinuous changes in the lowest σ–σ^* excitation energy in the silicon backbone around –40 °C and –10 °C.

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Dedicated to Prof. Hideki Sakurai on the occasion of his 70th birthday.

References and Notes

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6 For a review of optically active poly(dialkylsilylene)s, see M. Fujiki, *Macromol. Rapid Commun.*, **22**, 539 (2001) and references therein.

7 Polymer **5** was prepared by the Wurtz condensation of the corresponding dichlorosilane with the (*S*)-3,7-dimethyloctyl (Fluka, 96% ee)[4] and 2-ethylbutyl (Aldrich) substituents in 9% yield, according to the literature.[5]

8 All **1**–**5** may adopt a 7_3-helical conformation in solution. Recently, it was demonstrated that **4** takes the 7_3-helix in the solid state. See, J. Watanabe, H. Kamee, and M. Fujiki, *Polym. J.*, **33**, 495 (2001).

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