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On the Thermochromism of Polysilylene Copolymers of Highly Ordered Structure[1]

Kenkichi Sakamoto, Masaru Yoshida, and Hideki Sakurai*

Department of Chemistry, Faculty of Science, Tohoku University, Aoba-ku, Sendai 980, Japan

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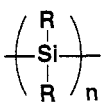
The existence of strong UV absorptions in polysilylenes is one of the main interests for these materials.[2] The absorption peak of dialkyl-substituted polysilylenes appears in the region from 300 to 325 nm in solution at room temperature. Thermochromism of the absorption is the most exotic property of this class of polymers.[3] The origin of the thermochromism is considered to be the conformational change of the polysilylene backbone between ordered and disordered forms occurring at low temperature. The change directly affects the degree of $\sigma-\sigma$ conjugation of the backbone and, consequently, the position of the UV absorption. Accordingly, structural regularity of the polymer plays an important role in the phenomenon. In fact, it has been known that only symmetrically or nearly symmetrically substituted alkyl polysilylene homopolymers **1**, such as poly(di-*n*-hexylsilylene), exhibit a sudden bathochromic transition occurring over a relatively small temperature range. On the other hand, unsymmetrically substituted polysilylene homopolymers **2** such as poly(*n*-hexylmethylsilylene) show a continuous red-shift of the absorption maximum with decreasing temperature until a limiting value is reached.[3b,4]



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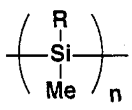

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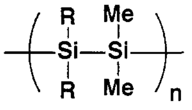

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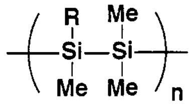

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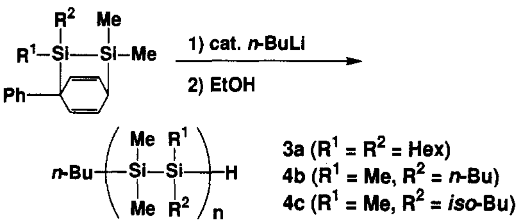
Recently, we have synthesized highly ordered alternating polysilylene copolymers **3** and **4** for the first time by the anionic polymerization of masked disilenes, 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-diene derivatives (eq 1).[5] We have noticed, without explanation, that copolymer **3a** (R = Hex) composed of two kinds of symmetrically substituted silylene units exhibits thermochromic behavior similar to the symmetrically substituted homopolymers.[5b,6] Herein we report the unprecedented thermochromic behavior of polysilylene copolymers **4** composed of both symmetrically and unsymmetrically substituted silylene units.[7]



(1)

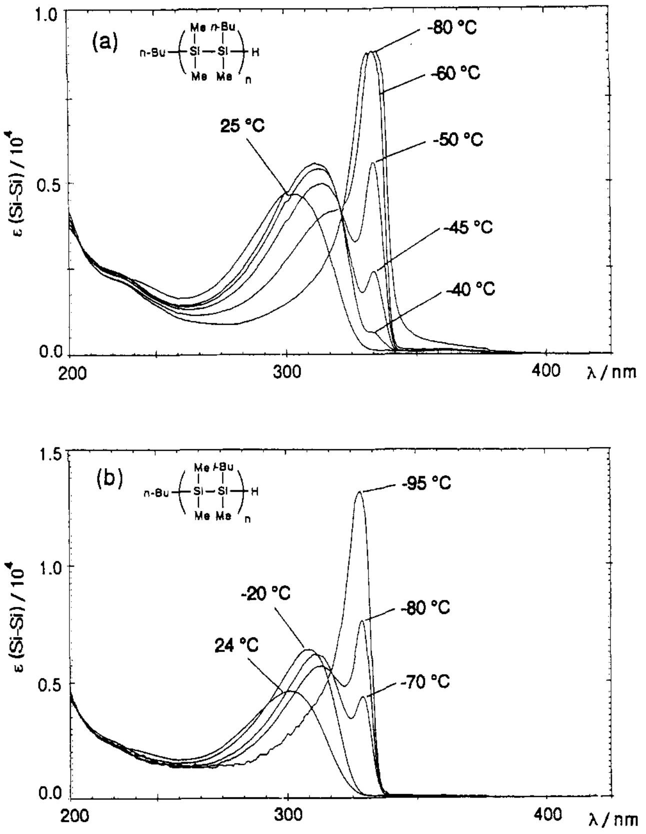
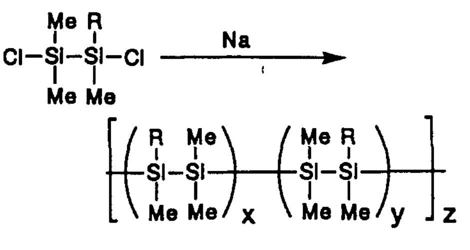


Figure 1. Temperature-dependent UV spectra of polysilylene copolymers (a) **4b** and (b) **4c** in 3-methylpentane.

We found that the alternating polysilylene copolymers **4b** (R = *n*-Bu) and **4c** (R = *iso*-Bu) also exhibited thermochromism with transition in solution similar to the symmetrically substituted polysilylenes. As shown in Figure 1, a new absorption appeared at 340 nm at a temperature below −40 °C for **4b**. Copolymer **4c** bearing a branched substituent requires a lower temperature to start the transition: a new peak starts to arise at 334 nm below −70 °C.

For the comparison, polysilylene copolymers **5b** and **5c** were prepared by sodium coupling of the appropriate dichlorodilanes (eq 2).[8] Polymers **5b** and **5c** have the same substituents as **4b** and **4c**, respectively, maintaining the same disilene unit in the polymer chains at least partly, but the sequences of the units were completely random as determined by ^{13}C NMR. Intriguingly, **5c** showed only a continuous small bathochromic shift, while **5b** showed thermochromism with a new absorption at 338 nm at a temperature below −90 °C (Figure 2). The intensity of the new peak increased even below −115 °C.



(2)

5b (R = *n*-Bu, 30 %), **5c** (R = *iso*-Bu, 15 %)

As mentioned above, hitherto the thermochromism has been observed only for symmetrically substituted polysilylenes. Moreover, it has been believed that branched alkyl substituents such as an isobutyl group inhibit the

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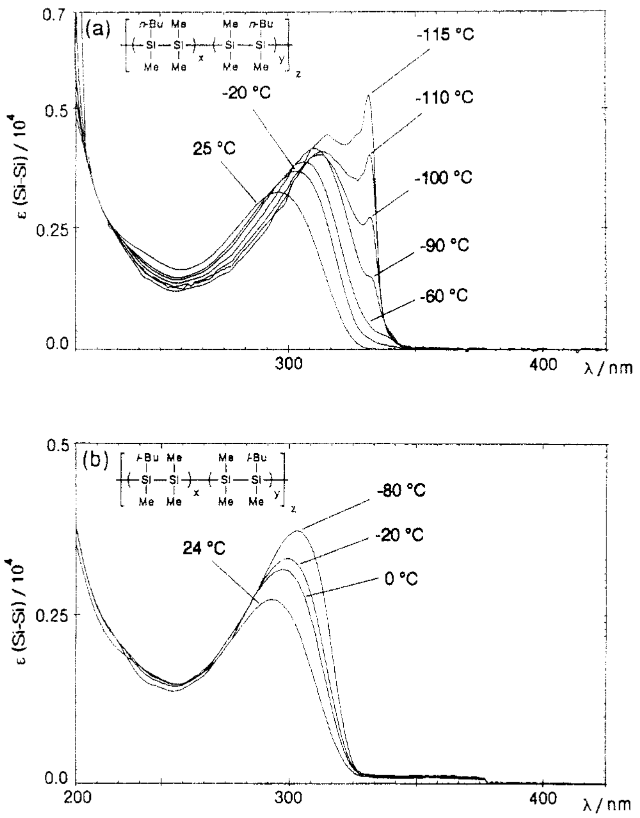

Figure 2. Temperature-dependent UV spectra of polysilylene copolymers (a) **5b** and (b) **5c** in 3-methylpentane.

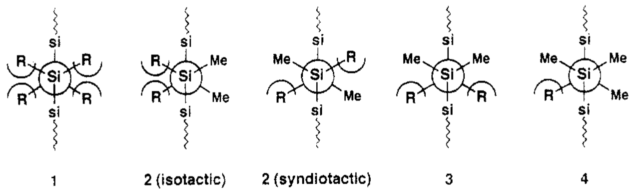

Figure 3. Newman projection for the trans segment of polysilylenes.

thermochromism.[4] However, the result undoubtedly demonstrates that polysilylene copolymers with unsymmetrical substituents, even involving branched chains, also show thermochromism with an apparent phase transition, provided that the polymers have an ordered alternating structure.

It has been proposed that thermochromism in solution is related to the increase of the relative population of trans polymer segments at low temperature.[3] Therefore, it is relevant to consider the conformational stability of the trans segments relative to others in the polymers. For this purpose, the Newman projection formulas for the trans segment of 1–4 are shown in Figure 3. In the trans segment, a pair of gauche interactions between alkyl substituents on the neighboring silicon atoms exists as shown in the figure. Gauche interactions involving the main chain are assumed to be insignificant here since silicon–silicon bonds are longer than silicon–carbon bonds, and, therefore, the steric repulsions involving the main chain should be much less substantial. The MM2 force field parameters for polysilanes determined by Allinger support the assumption.[9] The 3-fold torsional constants for Si–Si–Si–Si, C–Si–Si–Si, and C–Si–Si–C are reported to be 0.100, 0.300, and 0.633, respectively. These values are related to the magnitudes of rotational barriers around silicon–silicon bonds, being good indices for steric bulkiness. The values clearly indicate that repulsions between carbons on the neighboring silicon atoms are a controlling factor for the conformational stability.

For the trans segment of symmetrically substituted homo- and copolymers, **1** and **3**, the dominant two gauche interactions are even and balanced with each other, while the corresponding gauche interactions are uneven and unbalanced for unsymmetrically substituted copolymer **4**. Accordingly, the trans conformation responsible for thermochromism is more favored for both **1** and **3** than for **4**. Nevertheless, thermochromism observed for **4** occurred at very low temperature. This fact may be attributed to the lower degree of unevenness of the gauche interaction in **4** then in both **3** and **4**. In contrast with thermochromic polysilylenes, nonthermochromic unsymmetrically substituted homopolymer **2** has an atactic structure comprised of a random mixture of isotactic and syndiotactic connections of silylene units. The syndiotactic segments have two even gauche interactions between the methyl and hexyl groups, while the isotactic segments do not. The latter have two unbalanced gauche interactions: steric repulsions between the methyl groups and that of the hexyl groups. Then the trans arrangement should no longer be a stable conformer for this polymer.

For polysilylenes with all-trans structures, it is noteworthy that a small deviation of the backbone torsional angle from 180° resulted in a large change in the structure of the polymers. For example, polysilylenes with 7/3 helix structures have a torsional angle of 150°.[10] Thus, the uneven repulsion resulted in the destabilization of the all-trans structures and, consequently, in the inhibition of the thermochromic transition. Accordingly, *if pure syndiotactic homopolysilylene of **2** is synthesized, it would show the thermochromism.* This must be an extremely interesting challenge in polysilylene chemistry.

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(6) See also: Schilling, F. C.; Lovinger, A. J.; Davis, D. D.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* (a) **1992**, *25*, 2854; (b) **1993**, *26*, 2716.
(7) **4b**: $\bar{M}_n = 1.1 \times 10^5$, $\bar{M}_w = 1.7 \times 10^5$. **4c**: $\bar{M}_n = 1.1 \times 10^5$, $\bar{M}_w = 1.7 \times 10^5$. The sequence regularities of the polysilylenes were determined by ^{13}C NMR. The ratios of head-to-tail and head-to-head connections of the disilene units are 6:4 and 9:1 for **4b** and **4c**, respectively. The stereochemistry of the polysilylenes may be determined by the stereochemistry of the corresponding monomers, but at this moment no optical resolution was attempted.
(8) **5b**: $\bar{M}_n = 2.3 \times 10^4$, $\bar{M}_w = 5.6 \times 10^4$. **5c**: $\bar{M}_n = 7.7 \times 10^3$, $\bar{M}_w = 1.4 \times 10^4$.
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