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# A Correlation between Global Conformation of Polysilane and UV Absorption Characteristics

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When a mobile backbone conformation of $\pi$- and $\sigma$-conjugating polymers is strongly coupled with an electronic structure, changes in UV−vis absorption spectra and/or chiroptical properties are observed phenomenologically as thermochromism, solvatochromism, piezochromism, electrochromism, and/or mutarotation.[1,2] Although polysilanes, being $\sigma$-type chromophores, exhibit these phenomena to a remarkable degree, their structural origins are controversial because of the limited information available on the relationship among the conformational properties of the Si backbone, excited electronic state, and actual optical characteristics.[2] We found empirically for various polysilanes in THF at 30 °C that the lowest excitonic backbone peak intensity per silicon repeating unit, $\epsilon$ (Si unit/dm$^3$)$^{-1}$•cm$^{-1}$, increases exponentially as the viscosity index, $\alpha$, increases. The $\alpha$ value relates primarily to the conformational properties of the chain[3] and therefore in polysilanes to the mean free path of a photoexcited electron−hole pair. This correlation would be helpful for discussing the conformational change of polysilane in any condition. It would also be useful for predicting the lower and upper limits of the peak intensity for the respective globular and perfectly extended rod polysilanes.

Both optically active and inactive polysilanes, poly($R_1R_2Si$), have excellent optical characteristics for studying such conformational structures in solution, because it is known that the characteristics of the lowest excitonic Si($\sigma$)−Si($\sigma$*) absorption at 3−4 eV varies sensitively with the helical torsion angle, segmentation, and regularity of the helix.[4−6] On the basis of this understanding, we recently obtained various optically active and inactive polysilanes bearing chiral and achiral alkyl and/or phenyl pendants by Wurtz condensation of the corresponding substituted dichlorosilanes. The main features of these polysilanes in THF at 30 °C are that the $\epsilon$ value is broadly distributed from 5500 to 57 500 and the peak energy ranges from 3.5 to 4.2 eV ($\lambda_{max} = 290-352$ nm), while the $\alpha$ value ranges widely from 0.51 to 1.35.

Twenty-one polysilane samples were examined in this study: seven optically active poly(dialkylsilane)s with four different types of chiral $\beta$-, $\gamma$-, or $\delta$-branched alkyl substituents; eleven optically inactive poly(dialkylsilane)s with six different types of achiral $\beta$-, $\gamma$-, or $\delta$-branched substituents; an optically inactive poly(dialkylsilane) copolymer prepared from a racemic chiral monomer; and two optically inactive poly(alkylphenylsilane)s. These polysilanes were classified as having shrink coil, flexible coil, stiff, and rigid rodlike conformations from their $\alpha$ value[3] and $^{29}$Si-NMR line width.[6d] A shrink form with restricted segmental motion, which was suggested from the low $\alpha$ value of 0.5−0.6[6b] and broad $^{29}$Si-NMR line width of about 50 Hz,[6d] is forced by a pair of methyl and $\beta$-branched alkyl pendants.

Although the viscosity measurement needs a wide range of narrowly dispersed molecular weight polymer samples, today's advanced GPC instruments equipped with a viscosity detector enable us to measure the intrinsic viscosity, [$\eta$], as a function of the molecular weight of the polymer, $M$, in real time.[8] Despite the fact that the resulting information may be rather semiempirical compared to the chain radius of the gyration, $R_g$, determined by light scattering measurements, the $\alpha$ value tells us the degree of chain coiling directly.[3] The $\alpha$ value would be derived from the $R_g \propto M^{\nu}$ equation, where $\alpha = 3\nu - 1$. The $\alpha$ values of all poly($R_1R_2Si$) are listed in ref 8. Conventional **6** and **9** are in a flexible coil on the basis of light-scattering and viscosity measurements.[7,8]

Figure 1 plots the logarithm of the $\epsilon$ value and the peak width, the fwhm (eV), of polysilanes as a function of the $\alpha$ value in THF at 30 °C and shows good linear relationships between log($\epsilon$) and $\alpha$, $\epsilon = 1130 \exp(2.90\alpha)$, $r = 0.964$, and between log(fwhm) and $\alpha$, fwhm $= 3.15\exp(-2.77\alpha)$, $r = 0.963$. The product of $\epsilon$ and the fwhm, which corresponds to the oscillator strength of the peak, however, is almost independent of the global conformation. In addition, both the $\epsilon$ and fwhm values seem to be independent of the backbone peak energy, which is influenced by the helical torsion angle[4b] and $\sigma-\pi$ mixing effect between a phenyl ring and Si backbone.[4a]

Although the reason the $\epsilon$ and fwhm values vary exponentially with the $\alpha$ value is not perfectly clear, it is thought that both directly relate to the mean free path, $L$ in Si units, of a photoexcited electron−hole pair within its lifetime. This is because, if the electron−hole pair diffuses within a segment, the path will correspond to the segment length, which results

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(8) The [$\eta$]−M$^{\alpha}$ relations were measured at the Toray Research Center (Shiga, Japan) using a Waters 1500 GPC apparatus with a Viscotec H502a viscometer, whereas the $M$ values were typically distibuted from 10 000 to 4 000 000 because of unfractionated samples. See: Kinugawa, A. *TRC News* **1994**, *13*, 27. The compound number, $R_1$, $R_2$, and the $\alpha$ value are shown as follows: **1**, methyl, cyclohexylmethyl, 0.51; **2**, methyl, 2-ethylbutyl, 0.58; **3**, methyl, 2-methylpropyl, 0.59; **4**, methyl, (*S*)-2-methylbutyl, 0.59; **5**, methyl, *n*-propyl, 0.64; **6,** *n*-butyl, *n*-butyl, 0.71; **7**, 4-methylpentyl, 4-methylpentyl, 0.72; **8**, (*S*)-4-methylhexyl, (*S*)-4-methylhexyl, 0.72; **9,** *n*-hexyl, *n*-hexyl, 0.74; **10**, *n*-hexyl, (*S*)-4-methylhexyl, 0.75; **11**, methyl, phenyl, 0.79; **12**, *n*-hexyl, 3-methylbutyl, 0.80; **13**, *n*-hexyl, (*S*)-3-methylpentyl, 0.92; **14**, *n*-hexyl, phenyl, 0.99; **15**, *n*-hexyl, (*S*)-2-methyloctyl, 1.15; **16**, *n*-hexyl, 2-methylbutyl, 1.21; **17**, *n*-hexyl, (*S*)-2-methylbutyl, 1.25; **18**, *n*-hexyl, 2-ethylbutyl, 1.28; **19**, *n*-hexyl, 2-methylpropyl, 1.29; **20**, *n*-octyl, cyclohexylmethyl, 1.31; **21**, *n*-decyl, (*S*)-2-methylbutyl, 1.35. For the $\epsilon-\alpha$ relation study, we used only fractionated samples with a relatively high $M$ of over 100 000 because $\epsilon$ of both flexible[2a,7] and rodlike polysilanes[6c] tends to approach a constant value when the $M$ value exceeds about 10 000. Because the $\alpha$ values of stiff **12**, **13** , and **14** tend to decrease and attain about 0.6−0.7 over 1 000 000 of $M$, both the $\epsilon$ and $\alpha$ values were adopted at the peak $M$ of about 50000−100000.

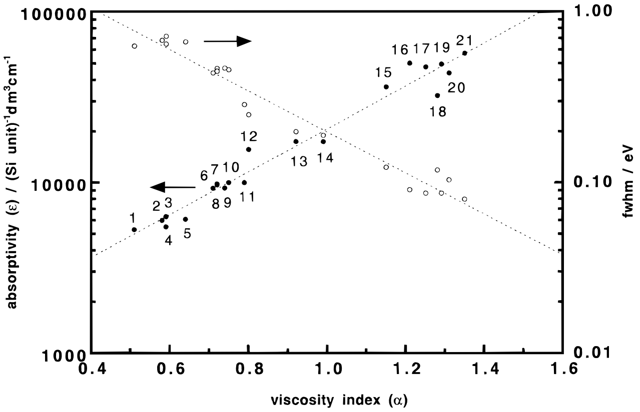

**Figure 1.** Lowest excitonic UV peak intensity, $\epsilon$, and full width at half-maximum, fwhm, of polysilanes as a function of the viscosity index, $\alpha$, in THF at 30 °C. Compound numbers are identical to those in ref 8.

in the $\alpha$ value in $[\eta] = \kappa M^{\alpha}$. Recently, an advanced one-dimensional exciton theory demonstrated that the exciton absorption greatly weakens and broadens as the degree of structural disorder increases.[4c] The disorders involve deviations in Si$-$Si bond length, Si$-$Si$-$Si bond angle, and Si$-$Si$-$Si$-$Si torsion angle. Such deviation would determine the segment length, the mean free path, or the effective $\sigma$-conjugation length. The $L$ value or segment length in Si repeating numbers is now estimated to be ~9 Si for **4** with $\alpha = 0.59$,[6b] ~30 Si for **9** with $\alpha = 0.74$,[7] and ~150 Si for **17** and **21** with $\alpha = 1.25-1.35$.[6c] These $L$ values may lead to the simple relation $\epsilon = 330L$, $r = 0.99$. As an application of these relationships, below we try to draw a picture of the structural change in the global conformation of polysilane.

The origin of the solution thermochromism of **9** has been controversial:[2a−d,f] Although **9** shows a broad absorption at room temperature, $\epsilon \sim 10\,000$, when the solution is cooled to $-30$ or $-55$ °C, it shows discontinuously a marked red shift of about 0.4 eV and an increase in peak intensity, $\epsilon = 25000-47000$, which is accompanied by a narrowing of 1/3 to 1/6. Previous studies attributed this change to coil-to-rod transition,[2c] the formation of microcrystals,[2d] an intrachain association with a trans-planar conformation,[2d] or aggregation.[2f] However, there is little direct evidence to prove these ideas because the solution thermochromism occurs at low temperatures. If the thermochromism is viewed in terms of the $\log(\epsilon)-\alpha$ and $\epsilon-L$ ralationships, it is reasonable to conclude that the increase in UV intensity results from a coil-to-rod transition (from $\alpha = 0.7$ to $\alpha = 1.1-1.3$) or from a short segment-to-long segment transition (from $L = 30$ to $L = 75-140$). The peak energy shift, meanwhile, may come from the helix-to-helix transition of an intrasegment, for example, from a $7_3$- to a $2_1$-helix, since the peak energy changes progressively with the helical torsion angle, as suggested from an *ab initio* calculations.[4b]

The piezochromism associated with the red-shifted UV band of **6** in the solid film occurs at high pressure.[2e] From the log(fwhm)$-\alpha$ relationship, this chromism could be attributed to the change from a $7_3$- to a metastable $2_1$-helical structure within the intrasegmental motion due to there being no sharpening of excitonic absorption. In optically active polysilane copolymers, the absorption intensity increases as the fraction of chiral silane increases, and the specific rotation of the copolymers increases as temperature decreases.[2f] The $\log(\epsilon)-\alpha$ relationship suggests that these increments result from the increase in helical segment length associated with the increase in the relative population of *P*- and *M*-helical segments.

By extrapolating the $\log(\epsilon)-\alpha$ relationship, the lower and upper limits of the peak intensity of polysilane in solution can be estimated for the two ultimate structures; $\epsilon = 1000$ for a globule ($\alpha = 0$), and $\epsilon = 150000-300000$ for a perfectly extended rod ($\alpha = 1.7-2.0$). Actually, it has been suggested that both poly(hydrophenylsilane) (**22**; $\epsilon = 2000$ in THF) and polysilanes with oligoether pendants ($\epsilon = 1100$ in EtOH) are in a tight random coil or a globule-like form.[9] When the H$-$Si bonding of **22** was replaced with sterically demanding alkyl$-$Si bondings by hydrosilylation, the absorption increased to $\epsilon = 5\,200$.[9a] This $\epsilon$ change may be due to a globule-to-coil transition. Conversely, the $\epsilon$ value for **19** ($M_w = 2 \times 10^6$) in isooctane progressively increases from 45 000 with an fwhm of 0.10 eV at 3.86 eV to 110 000 with an fwhm of 0.05 eV at 3.91 eV when the temperature is cooled from +25 to $-75$ °C.[6d] This $\epsilon$ value, the highest among all polysilanes, would correspond to an almost perfect rod structure with $L$ of ~330 and $\alpha = 1.6$.

The $\epsilon-\alpha$, fwhm$-\alpha$, and $\epsilon-L$ relationships in the Si$-$Si absorption characteristics are very sensitive probes for studying global conformation, and this information will be very helpful in advancing discussions on the structural origins of various chromisms and/or mutarotations in other polysilanes because many structural changes have already been postulated.[2]

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