Effect of main chain length in the exciton spectra of helical-rod polysilanes as a model of a 5 Å wide quantum wire

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Helical polysilane rods were regarded as a soluble, polymeric model of a quantum wire with a ~5 Å width. Spectral characteristics of the lowest exciton band of the helix located at ~4 eV in isoctane at 20 °C were first measured as a function of a wire length varying from ~5 Å to ~3000 Å. Both the extinction coefficient and the circular dichroism coefficient were found to tend to increase linearly as the logarithm of the wire length increases, whereas the exciton energy and the spectral band width approached limiting values. © 1994 American Institute of Physics.

Much effort in recent semiconductor physics has been devoted to understanding excitons in quantum wire (QWR) structures intended for high-performance photonics materials exhibiting nonlinear optical (NLO), photoluminescence (PL), and electroluminescence properties. Such QWR systems include artificial GaAs/AlAs crystal surfaces, porous Si, \( \pi \)-conjugating polymers, and cyanine-dye \( J \) aggregates. Most theoretical and experimental works on ground and excited electronic states of the QWR structures, however, focus on wire width dependence, but not on wire length dependence.

Chain-like organopolysilane (OPS), consisting of a Si skeleton and organic substituents, is regarded as a soluble, \( \sigma \)-conjugating polymer model for QWRs with a several Å wire width. For example, poly(di-n-hexylsilane) (PDHS), having a trans-planar skeleton in the solid film or in a glassy solution at low temperature, exhibits excitonic UV absorption with a binding energy of about 1 eV. It has highly efficient PL due to the main chain (not side chain) at 3–4 eV.\(^{10,11}\) The band calculation for an idealized OPS having an infinite main-chain length originally suggests full conjugation of the Si \( \sigma \) electron along the whole main chain.\(^{12}\) However, in actual OPSs, including PDHS, both structural disorders due to a floppy main chain in the fluid solution, and a finite main chain length, could lead to a Si \( \sigma \)-conjugating state which is limited to within 10–20 Si atoms.\(^{13,14}\) As a result, most OPSs exhibit very broad, 0.5–0.6 eV wide absorption and a narrow, 0.2 eV wide PL,\(^{8}\) arising from its segment-like or worm-like QWR structure.\(^{15}\)

Recently we have found a new class of optically active, chiral OPSs with a high molecular-weight fraction, poly(n-decyl((S)-2-methylbutyl) silane) (OPS-1).\(^{16}\) This maintains a clockwise-screw-sense and a rigid helical-rod structure even in solutions at room temperature. The exact structure of this helix is now uncertain, but if the structure is assumed to be \( \frac{7}{3} \) helix as found in several OPSs in solids, this helix corresponds to a QWR having a ~5 Å diameter, considering van der Waals radius of helical silicon atoms. Several spectroscopic features of OPS-1 differed significantly from those of the conventional, optically inactive OPSs: (1) its normalized lowest exciton intensity, \( \epsilon \approx 55000 \) (Si unit/liter)\(^{-1}\) cm\(^{-1}\) at 3.85 eV, was 5–10 times greater and its full width at half maximum (FWHM) value, 0.10 eV, diminished by 1/4–1/6: (2) the PL spectral profile was completely a mirror image of the 3.85 eV exciton band. The lowest exciton circular dichroism (CD) spectrum at 3.82 eV characteristic of clockwise-screw-sense, uniform helical Si skeleton, also, matched the corresponding 3.85 eV absorption.\(^{16}\) A very similar rigid helical-rod structure can also be seen in other chiral OPS homologues: poly(n-alkyl((S)-2-methylbutyl)silane), where \( n \)-alkyl is from \( n \)-propyl to \( n \)-decyl.\(^{10}\) These results encourage us to examine inherent excitonic features of helical OPS systems more precisely as a function of main-chain length, which corresponds to QWR length, in isotropic media at room temperature for neglecting interaction between Si skeletons. In this letter, we report first the main-chain length dependence on the exciton spectroscopic features of the OPS helical rod itself in dilute solution at room temperature, without any interchain and intrachain interactions.

The helical OPSs used were obtained by a sodium-mediated condensation of dichlorosilane bearing both (S)-2-methylbutyl and \( n \)-alkyl substituents in hot toluene with 15-crown-5.\(^{16}\) The yields of these polymers were typically 7–20% after fractional precipitation with toluene-ethanol mixed solvent. Chemical structures of helical OPSs are shown in Fig. 1.

Figures 2(a) and 2(b) show the UV, CD, PL, and PL excitation (PLE) spectra of poly(n-hexyl((S)-2-methylbutyl)silane) (OPS-2H) in isoctane at 20 °C. The wire length was roughly estimated from the product of the effective Si-Si bond length (1.8 Å) and the weight-average Si repeating number \( (P_w) \). The CD band at 3.82 eV matches the 3.85 eV UV band and the PL spectral profile at 3.79 eV is completely a mirror image of the exciton UV and CD band. The PLE band at 3.86 eV almost traces the 3.85 eV UV and CD bands. Although these spectroscopic features of OPS-2H are very similar to those of OPS-1 whose structure is homogeneous and has only one excitation energy state at ~3.9 eV, its nor-

![FIG. 1. Chemical structures of helical OPSs used in this work.](image-url)
normalized absolute absorptivity, $\varepsilon=38,000$ and normalized absolute CD intensity, $\Delta e=7.9$, are slightly lower than those of OPS-1 with $\sim 3000$ Å wire length. While Kuhn's dissymmetry factor ($g=\Delta e/e$) of OPS-2H, $2.0\times10^{-4}$, is almost identical to that of OPS-1, the discrepancy is suspected to arise from the difference in the wire length of OPS-1 and OPS-2H, not side-chain length. This is because the dissymmetry factor could be sensitive to change in helical conformation of enantiomerically pure solute in isotropic media. The dissymmetry factor is theoretically interpreted as $g=4RD^{-1}$ $=4|\mathbf{m}||\mu|\cos\theta (|\mathbf{m}|^2+|\mu|^2)^{-1}$ where $R$ is the rotational strength, $D$ is the dipole strength which is closely related to the oscillator strength—both $R$ and $D$ are normalized as Si unit/liter—and $\theta$ is the angle between the magnetic and electric transition moments $\mathbf{m}$ and $\mu$. Since the term $|\mathbf{m}|^2$ is negligibly smaller than $|\mu|^2$, then $g=4 |\mathbf{m}||\mu|^{-1}\cos\theta$. This idea is supported by results from a short wire length sample of OPS-2L ($L=28$ or 50 Å of wire length), which is isolated by fractional precipitation of the mother liquor: although both absorptivity, $\varepsilon=28,000$, and CD intensity, $\Delta e=4.8$, are lower than those of OPS-2H, the dissymmetry factor of OPS-2L, $1.7\times10^{-4}$, is almost identical to that of OPS-2H, following the unchanged values of $\mathbf{m}$, $\mu$, and $\theta$.

Figures 3(a), 3(b), and 3(c) illustrate the lowest exciton characteristics of all fourteen samples isolated from the nine helical OPS derivatives mentioned above, as a function of the logarithm of the wire length in isooctane at 20 °C. Here we emphasize that from Fig. 3(b) the helical Si skeleton in this series of helical OPSs is basically isostructural, since Kuhn's dissymmetry factor, $g=\Delta e/e=1.82(\pm0.22)\times10^{-4}$—which varies with the magnitudes of $|\mathbf{m}|$, $|\mu|$, and $\theta$ associated with helical structure—is almost independent of both main-chain length and $n$-alkyl side-chain length.

Interestingly, the respective values of both the normalized lowest exciton extinction coefficient and the normalized lowest exciton CD coefficient tend to increase linearly, as the logarithm of the wire length increases, and do not seem to converge to constant values. This novel $e$-length relationship can be compared with that for poly(n-dodecyl-methylsilane) (PDMS). In the case of PDMS, the value of $e$ tended to saturate at a limiting value, $e\sim5,000$, at around 75–100 Å wire length. This discrepancy could relate to the stiffness of the main chain due to the different side-chains. Previous studies by light-scattering and intrinsic viscosity-molecular weight of polymer ($\eta$-$M$) measurements indicate that most di-alkyl-substituted OPSs in solutions at room temperature—including PDMS and PDHS, of which substituents are sterically flexible structures—take on worm-like disordered structures or collective structures of relatively short $\sim 30$ Å long segments. In contrast, we conclude from the excitation-energy dependence of PL anisotropy study that the helical OPSs in this work maintain their rigid-rod structure.
even in solutions at room temperature.\textsuperscript{16} This arises from the sterically hindered $\beta$-branched chiral substituent. This view is further supported by $[\eta]-M^n$ relationship (in tetrahydrofuran at 30 °C),\textsuperscript{19} while the exponential factor ($\sim$ the viscosity index), $a$, is known to vary with the degree of polymer chain coiling.\textsuperscript{20} Here OPS-\textbf{2H} and OPS-\textbf{1} give $a=1.25$ and 1.35, respectively, and the values are empirically classified to be rigid-rod polymer, while PDHS gives $a=0.78$, which is typical for a flexible polymer.

To explain the $e$-length relationship, we assume that the total dipole strength (or the total oscillator strength) of excitons and interband transitions is independent of the wire length: as the wire length increases, the dipole strength of the lowest exciton transition increases progressively along with suppression of the higher-order excitons and interband transitions. This is due to redistribution of the total strength. The relative dipole strength of these transitions eventually would saturate a theoretical limit of an idealized infinite QWR.\textsuperscript{21} Actually, an integration of all absorption of the helical OPSs ranging from 3.5 to 6.2 eV, which is indicative of the total oscillator strength, depends only slightly on the wire length. Similarly, this idea may be applicable to the wire length dependence on the rotational strength. Thus, the nonconvergent features of $e$-length and $\Delta e$-length relationships are thought to be mesoscopic features varying from very short wire to infinite wire.

Much theoretical and experimental interest is being focused on the enhancement of NLO susceptibility. Compared with the conventional $\pi$-conjugating organic NLO polymers and structurally disordered OPSs, the extraordinarily intense and narrow exciton peak appearing in the helical OPSs may further enhance third-order NLO susceptibility. Recent theoretical calculations suggest that the magnitude of third-order NLO susceptibility in a finite QWR system without terminals increases by a power law of the wire length up to 200 Å long.\textsuperscript{9} Moreover the third harmonic generation spectrum significantly sharpens and its intensity markedly increases, likewise linear absorption spectrum, as structural disorders in a linear semiconducting polymer disappear.\textsuperscript{22}

Figure 3(c) plots the values of the lowest exciton energy ($E_{\text{max}}$) and the FWHM of the exciton absorption in the helical-rod OPSs in isooctane at 20 °C, as a function of the logarithm of the wire length. When the wire length is over $\sim$200 Å, the value of $E_{\text{max}}$ lowers gradually from 3.95 eV to 3.85 eV, and the value of FWHM diminishes from 0.15 eV to 0.10 eV. These features are similar to the previous data for flexible PDMS.\textsuperscript{19} Although this convergence of the $E_{\text{max}}$-length relationship has already been simulated by a simple Sandorfy C model for finite OPS chain with trans-planar conformation,\textsuperscript{23} there seems to be little work on the FWHM-length relationship; the Sandorfy approximation derived from a difference in resonance integrals of geminal and vicinal sp$^3$ hybrid molecular orbitals in Si-Si-Si bonds neglecting the exciton effect, which empirically gives the lowest transition energy as a function of the Si-Si bond repeating numbers in an analogy with bond-alternated finite polyenes with terminal ends. We now consider that the wire length saturated at $\sim$200 Å is related to the movement of an electron-hole pair within its lifetime confined in present helical OPS systems.

In summary, we have measured the lowest exciton band characteristics located at $\sim$4 eV of one-screw-sense, rigid-rod, helical polysilanes in isooctane at 20 °C, as a function of the main-chain length. Both the extinction and circular dichroism coefficients were found to tend to increase linearly as the logarithm of the main-chain length increases, while the respective values of exciton energy and spectral width of the band converged to limiting values. The helical polysilanes are a suitable and promising model of a $\sim$5 Å wide QWR with varying length. These results encourage us to elucidate intrinsic nonlinear optical and charge-transport properties of the helical polysilane compared to those of the segmented or worm-like polysilane reported previously.

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