# Experimental Evidence for Helical Conformation of Poly(methylphenylsilylene) in Solution

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This paper describes a simple methodology designed to prove that poly(methylphenylsilylene) (**1**) in solution has a helical conformation by a comparing the optical properties of optically inactive **1** with those of its optically active copolymer derivative. This approach can clarify the main-chain conformation from spectroscopic evidence.

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Knowledge of the main-chain conformations (MCCs) of polymers in solution is vital for controlling their intrinsic physicochemical properties. Although well-established light scattering and viscosity measurements provide information on global shape such as the radius of gyration and the viscosity index (α),[1,2] these methods cannot determine whether a local conformation is helical and/or regular. In this study, we propose a simple methodology which uses polysilylenes to confirm whether or not the conformation of chromophoric polymers in solution is helical as described below. The optical properties of polysilylenes in the UV-VIS range are known to be strongly related to their MCC because they are associated with σ-electrons delocalized along their main-chain.[3] Poly(methylphenylsilylene) (**1**) is one of widely-studied polysilylenes and exhibits such optoelectronic properties as high hole-drift-mobility,[4] photochemical hole burning,[5] and electroluminescence.[6,7] The MCC of **1**, however, was not fully understood because the main-chain peak energy ($E_{peak}$) depends not only the main-chain conformation[8] and the Si repeating number[9] but also on the effect of σ–π mixing between the phenyl groups and the Si main-chain.[10] In this study, we show the first experimental evidence that optically inactive **1** has a helical MCC by comparing the optical properties of **1** with those of its optically active copolymer derivative and $^{29}$Si NMR spectra.

We prepared polymer **1** by a conventional Wurtz-type reaction involving methylphenyldichlorosilane (Shin-Etsu) and a sodium lump in dry toluene at 65°C in an Ar gas atmosphere. The isolated yield of **1** with $M_w$=44000 was 4.2%. We obtained the copolymer, poly{(methylphenylsilylene)$_{0.95}$-*co*-((*S*)-2-methylbutylphenylsilylene)$_{0.05}$} (**2**), in a similar way by copolymerization with a methylphenyldichlorosilane/(*S*)-2-methylbutylphenyldichlorosilane nominal molar feed ratio of 95/5. The molecular structures of **1** and **2** are shown in Figures 1 and 2, respectively. The isolated yield of **2** with $M_w$ = 32000 was 3.8%. The (*S*)-2-methylbutylphenylsilylene content in **2** was 4.8% based on the peak ratio between $SiCH_3$ from methylphenylsilylene units and $CH_3C^*H(C_2H_5)CH_2Si$ from (*S*)-2-methylbutylphenylsilylene units by $^1$H-NMR (300 MHz, $CDCl_3$).

Figures 1-3 show the UV absorption, fluorescence (FL), and fluorescence anisotropy (FLA) spectra of **1** and **2**, and the circular dichroism (CD) spectrum of **2** in tetrahydrofuran at 23-25°C. In Figures **1** and **2**, the intense broad UV absorption at 3.6 eV (335 nm) is assigned to the Si σ-Si σ$^*$ transition whose dipole moment is parallel to the main-chain axis and the weak broad absorption at 4.3 eV (288 nm) is assigned to the phenyl π-phenyl π$^*$ transition whose dipole moment is perpendicular to the main-chain axis. The 3.6-eV UV peak intensity, ε, reached 8200 (Si-repeating unit)$^{-1}$dm$^3$cm$^{-1}$ for **1** and 7100 (Si-repeating unit)$^{-1}$dm$^3$cm$^{-1}$ for **2**. In Figure 3, the spectral profile and extremum of the positive Cotton CD band at 3.6 eV (340 nm) is almost identical to that of the 3.6 eV-UV absorption band in Figure 3, whereas those of the negative Cotton CD band at 4.35 eV (285 nm) almost match those of the 4.3 eV-UV absorption in Figure 3. The spectral profiles of the sharp FL band at 3.5 eV (354 nm) of both **1** and **2** no longer trace a mirror image of either the 3.6 eV-UV or 3.6 eV-CD band. Additionally, the FLA spectra in the 3.6 eV-UV band of both **1** and **2** are changed from about 0.3 at 3.6 eV to almost zero at 4.2 eV.

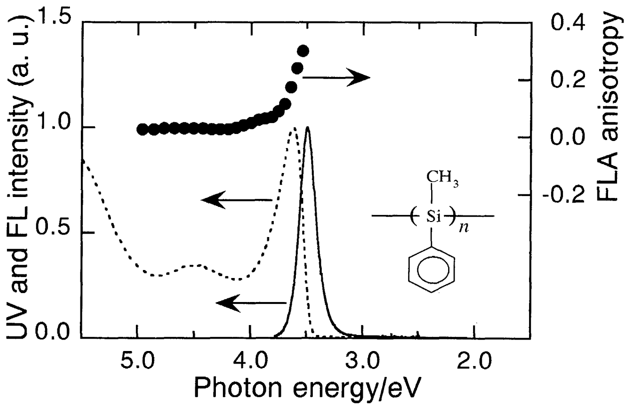

**Figure 1.** Normalized UV absorption spectrum (dotted line), FL spectrum excited at 4.5 eV (solid line), and FLA spectrum monitored at 3.5 eV (filled circles) in tetrahydrofuran at 23-25°C and molecular structure of **1**.

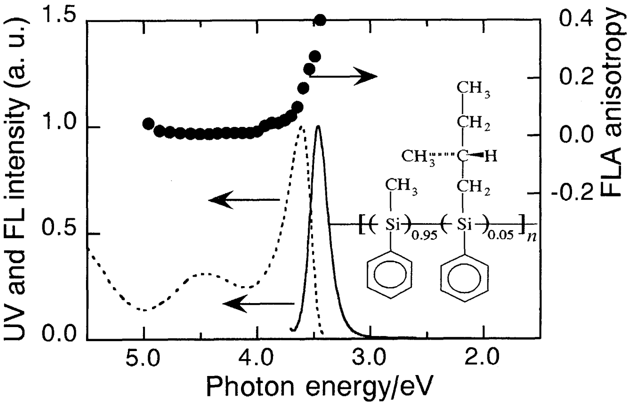

**Figure 2.** Normalized UV absorption spectrum (dotted line), FL spectrum excited at 4.5 eV (solid line), and FLA spectrum monitored at 3.5 eV (filled circles) in tetrahydrofuran at 23-25°C and molecular structure of **2**.

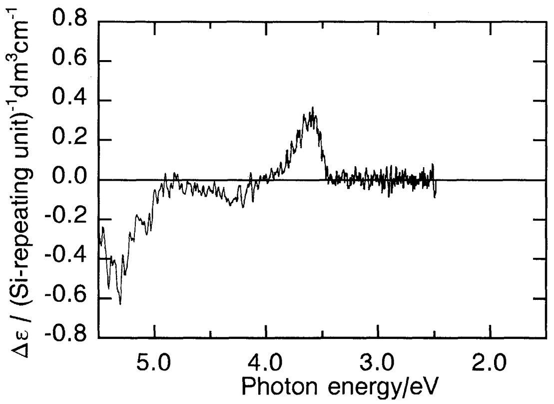

**Figure 3.** CD spectrum of **2** in tetrahydrofuran at 23-25°C.

The UV, CD, FL, and FLA spectroscopic features of **2** are consistent with the following ideas. (1) The most stable local molecular conformation of **2** is helical with a preferential screw-sense. This is because, if **2** has an achiral and trans-planar conformation, no Cotton CD signal should be observed. If part of **2** has a trans-planar moiety which is not responsible for the CD signal incorporated in the main chain, the CD spectrum will not completely match the UV spectrum. (2) The MCC of **2** is a collection of several types of single-screw-sense helical segments that includes screw pitches and/or segments with several different lengths. Such irregular helical structures could result in broad 3.6 eV-UV and -CD bands that could convolute into several UV and CD components.[11] This is because, if the CD band of **2** comes ideally from the single-excitation state of single-screw-sense, single-screw-pitch segments, the FL band should trace a mirror image of both the 3.6 eV-UV and -CD bands, as previously demonstrated in a poly(n-alkyl(*S*)-2-methylbutylsilylene) series.[12] (3) The global conformation of **2** is in a random-coil state consisting of several types of helical segment. The FLA result indicates that the relative arrangement of the absorbing and emitting chromophores of **2** is not collinear. The existence of many local broken geometries incorporated in the Si main-chain will result in the overall global shape being in a random-coil state. The global shape with random-coils of **2** is consistent with an idea arising from the $\varepsilon-\alpha$ correlation, reported previously.[12] The stereochemical configuration of **2** is almost identical to that of **1**,[13] because the triad proportion of the three well-resolved, prominent $^{29}$Si NMR peaks at - 39.3 (*it*), - 39.9 (*st*), and - 41.3 ppm (*ht*) of **2**[13] is almost identical to that of 1.[14] A small amount of (S)-2-methylbutyl-phenylsilylene entity induces only a slight population imbalance in the *P*- and *M*-helical components included in optically inactive **1**. This indicates that such a small amount of chiral silane moiety incorporated in **1** does not significantly affect the microtacticity, or the UV absorption, FL, and FLA characteristics of **1**, except for the appearance of the CD signals of **2**. All the features of the UV peak intensity, $E_{peak}$ of the UV and FL bands, and FLA characteristics in **2** are almost consistent with those in 1 except for the CD signals of **2**. The local helical conformation of **1**, therefore, is almost the same as that of **2**. These results and considerations lead to the conclusion that **1** in solution has a random-coil conformation consisting of a mixture of irregular *P*- and *M*-helical segments but not trans-planar segments.

The idea that the most stable conformation of **1** is helical is further supported by a force-field calculation using Discover III (MSI, ver 3.00, the PCFF force-field). The respective *P*- and *M*-helical conformations near 160° and 200° are more stable than a trans-planar conformation at 180°. This slowly winding helical feature seems to be independent of *it*-, *st*-, and *at*- oligomers of **1**. The barrier height between the *P*- and *M*-helical states of *it*-, *st*-, and *at*- oligomers of **1** reached 20-25 Kcal/mol.

In conclusion, we showed experimental evidence for the idea that optically inactive **1** has a randomly coiled helical main-chain by comparing the optical properties of **1** and optically active copolymer **2** and by comparing the $^{29}$Si NMR spectra of **1** and **2**. The conformational analysis described above is very promising for identifying the local conformation of other optically active chromophoric polymers.

## References and Notes

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