

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

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(Received March 16, 1999; CL-990177)

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.

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 conformation⁸ and the Si repeating number⁹ 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 ²⁹Si 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 SiCH₃ from methylphenylsilylene units and CH₃C*H(C₂H₅)CH₂Si from (S)-2-methylbutylphenylsilylene units by ¹H-NMR (300 MHz, CDCl₃).

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-

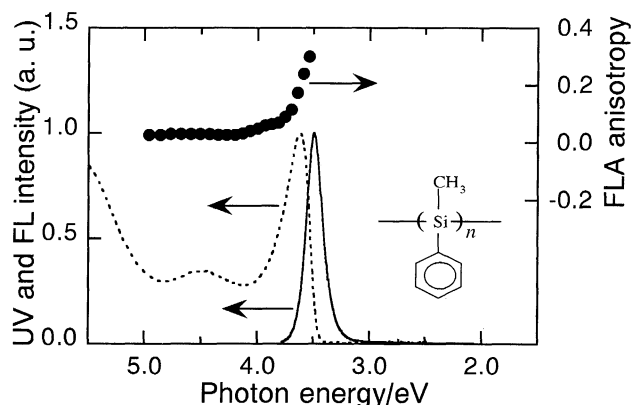


Figure 1. Normalized UV absorption spectrum (dotted line), FL spectrum excited at 4.5 eV (solid line), and FLA spectrum monitored at 3.5 eV (filled circles) in tetrahydrofuran at 23-25°C and molecular structure of **1**.

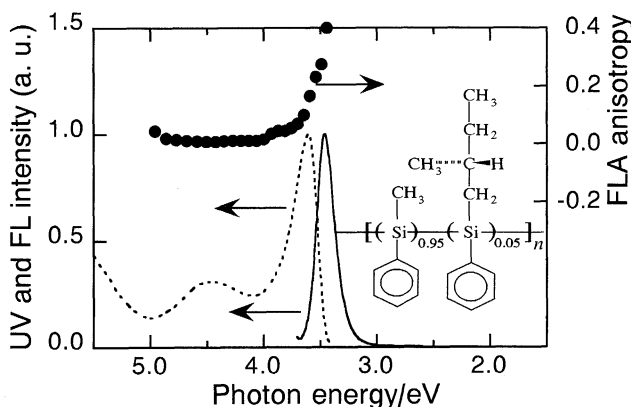


Figure 2. Normalized UV absorption spectrum (dotted line), FL spectrum excited at 4.5 eV (solid line), and FLA spectrum monitored at 3.5 eV (filled circles) in tetrahydrofuran at 23-25°C and molecular structure of **2**.

chain axis. The 3.6-eV UV peak intensity, ϵ , reached 8200 (Si-repeating unit)⁻¹dm³cm⁻¹ for **1** and 7100 (Si-repeating unit)⁻¹dm³cm⁻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.

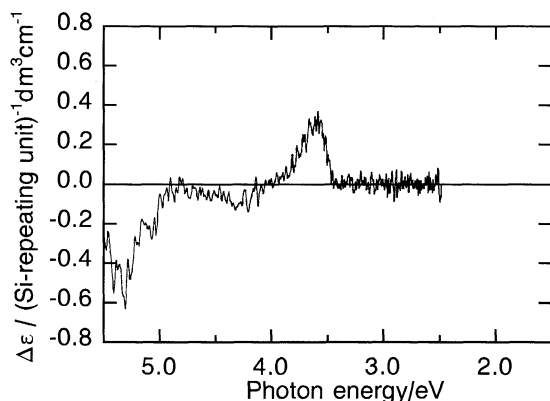


Figure 3. CD spectrum of **2** in tetrahydrofuran at 23-25°C.

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 ϵ - α 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 ²⁹Si 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 ²⁹Si 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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- 1 I. A. Katime and J. R. Quitana, in "Comprehensive Polymer Science," ed by C. Booth and C. Price, Pergamon, Oxford (1989), Vol. 1, Chap. 4.
- 2 P. A. Lovell, in "Comprehensive Polymer Science," ed by C. Booth and C. Price, Pergamon, Oxford (1989), Vol. 1, Chap. 9.
- 3 K. Takeda, H. Teramae, and N. Matsumoto, *J. Am. Chem. Soc.*, **108**, 8186 (1986).
- 4 M. A. Abkowitz, F. E. Knier, H. -J. Yuh, R. J. Weagley, and M. Stolka, *Solid State Commun.*, **62**, 547 (1987).
- 5 Y. Ohsako, J. R. G. Thorne, C. M. Phillips, R. M. Hochstrasser, and J. M. Zeigler, *J. Phys. Chem.*, **93**, 4408 (1989).
- 6 A. Fujii, K. Yoshimoto, M. Yoshida, Y. Ohmori, K. Yoshino, *Jpn. J. Appl. Phys.*, **34**, L1365 (1995).
- 7 Y. Xu, T. Fujino, H. Naito, K. Oka, and T. Dohmaru, *Chem. Lett.*, **1998**, 299.
- 8 R. D. Miller and J. Michl, *Chem. Rev.*, **89**, 1351 (1989).
- 9 J. E. Mark, H. R. Allcock, and R. West, in "Inorganic Polymers," ed by P. Hall and E. Cliffs, NJ (1992), Vol. 1, Chap. 5.
- 10 H. Teramae and K. Takeda, *J. Am. Chem. Soc.*, **111**, 1281 (1989).
- 11 M. Fujiki, *J. Am. Chem. Soc.*, **116**, 6017 (1994).
- 12 M. Fujiki, *J. Am. Chem. Soc.*, **118**, 7424 (1996).
- 13 J. Maxka, F. K. Mitter, D. Powell, and R. West, *Organometallics*, **10**, 660 (1991).
- 14 Unpublished results.