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 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.

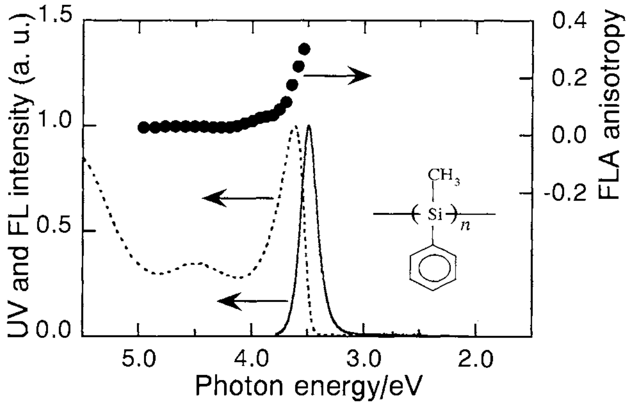

Figure 1. Normalized UV absorption spectrum (dotted line), FL spectrum excited at 4.5 eV (solid line), and FLA spectrum monitored at 3.5 eV (filled circles) in tetrahydrofuran at 23-25°C and molecular structure of **1**.

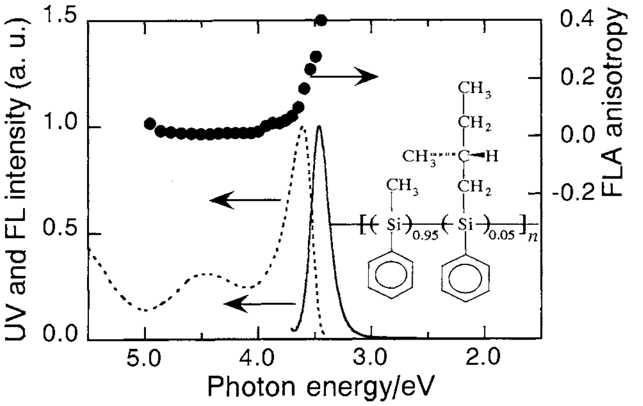

Figure 2. Normalized UV absorption spectrum (dotted line), FL spectrum excited at 4.5 eV (solid line), and FLA spectrum monitored at 3.5 eV (filled circles) in tetrahydrofuran at 23-25°C and molecular structure of **2**.

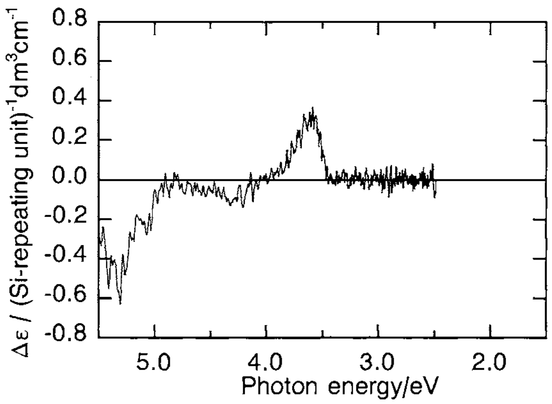

Figure 3. CD spectrum of 2 in tetrahydrofuran at 23-25°C.

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 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 ^{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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14 Unpublished results.