Origin of Broad Visible Photoluminescence from Poly(alkylarylsilylene) Derivatives

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ABSTRACT: We investigated the absorption, photoluminescence (PL), and PL anisotropy spectra of a variety of poly(alkylarylsilylene)s in solution at room temperature and in thin film form in the 20−296 K range. The poly(alkylarylsilylene)s include poly(methyl-*p*-*tert*-butylphenylsilylene) (**1**), poly(methylphenylsilylene) (**2**), poly(ethylphenylsilylene) (**3**), poly(*n*-pentylphenylsilylene) (**4**), poly(*n*-hexylphenylsilylene) (**5**), and poly(*n*-pentyl-*m*-tolylsilylene) (**6**). Although there was always a visible PL band from **1**, **2**, and **3** in the visible region, there was almost no visible PL band with thin films of **4**, **5**, and **6** in the room temperature to 20 K range. We ascribe the difference in the PL characteristics to the extended global shape with a spatially homogeneous local conformational structure in solution and in solid films.

Introduction

Much attention has been paid to light-emitting conjugated polymers in recent years because of their possible applications as, for example, electroluminescence (EL) devices and lasing materials.[1−7] Polysilylenes are candidate materials for this purpose because of their intense excitonic absorption, highly efficient PL and EL emission in the 3−4 eV range,[7] photoconductivity,[8] and high electron and hole carrier mobilities.[9] Among various polysilylenes, poly(alkylarylsilylene) (PAAS) derivatives are promising as regards realizing high-performance EL devices because of their high glass transition temperatures and thin film forming ability.

Polysilylene **2**, a typical PAAS, invariably exhibits unusual dual bands in films at low temperature: a sharp, near-UV PL (U-PL) or EL band at 3.5 eV and an intense broad, visible PL (V-PL) or EL band near 2.7 eV.[7,10] The dual PL bands have long been believed to be characteristic of all PAAS derivatives because of their chemical and electronic structural similarities. It has been suggested that **2**, prepared by the Wurtz coupling reaction with an alkali metal and methylphenyldichlorosilane, may contain a small number of skeleton branching defects.[11] Some poly(methylphenylsilylene)s containing substituents in the para and meta positions of the phenyl substituents have been recently reported to show no detectable V-PL although their PL spectra have been measured in solution at room temperature.[12] Although the first EL device based on **2** was reported several years ago,[7] the EL band appeared mainly in the visible region, together with an EL band in the UV region. Recent improvements in the chemical synthesis of **2** have led to an EL device whose UV emission dominates, but which retains a weak visible emission. Other recent studies on the hole transport properties of polysilylenes by microwave absorption and dc time-of-flight techniques[13,14] have revealed that, as the density of the silicon-based defects increases, the charge carrier mobility decreases exponentially, and the electron−phonon binding energy also increases, saturating at 0.85 eV for radical cations and at 0.95 eV for radical anions.[15]

In line with this idea, we recently showed that **4** with fewer branching defects exhibits only the U-PL band in thin film and in THF solution without any observable V-PL band.[16] Although the photophysical properties are ascribed predominantly to the electronic transition involving the extensively delocalized σ-electrons along the silicon backbone, these results strongly suggest that several of the optical and electrical properties of PAAS derivatives might be governed by structural defects and are possible to control by changing the degree of steric hindrance of the substituents. We require a more systematic study of the chemical structure of PAAS derivatives and the UV-PL characteristics to obtain a single UV-EL emission in devices based on polysilylenes.

Here, we describe how the absorption, PL, and photoluminescence anisotropy (PLA) characteristics of PAAS are influenced by the modification of the substituents on the Si atoms and the peripheral phenyl ring position. We found a good relationship between the V-PL and UV absorption-PL characteristics of PAAS and a simple way to reduce the V-PL of PAAS derivatives by modifying the substituents.

Experimental Section

General. ^{13}C (75.43 MHz) and ^{29}Si NMR (59.59 MHz) spectra were obtained in $CDCl_3$ at 30 °C with a Varian Unity 300 spectrometer using tetramethylsilane as an internal standard. We determined the weight-average (M_w) and number-average molecular weights of the polymer (M_n) using gel permeation chromatography (Shimadzu A10 instruments, Shodex KF806M), based on a calibration with polystyrene standards. Differential scanning calorimetric data were recorded on a Seiko EXTAR 6000 in an N_2 atmosphere at a scan rate of 10 K/min. We formed a thin polysilylene film, $\sim 0.1\ \mu$m thick, on a quartz plate from a toluene solution by spin-coating and overnight drying in a vacuum. We obtained the UV spectra of the polymers in tetrahydrofuran with a Hitachi U3500 spectrometer at room temperature. We recorded the PL, PL excitation, and PL anisotropy (PLA) spectra in toluene on a Hitachi F850 spectrofluorometer at room temperature. We measured the low-temperature UV absorption and PL spectra in the solid-state film with the U3500 and F850 instruments, respectively, both equipped with a cryostat (Daikin Cryokelvin).

Monomer Synthesis. Dichloro-*n*-hexylphenylsilane was prepared by the condensation of phenyl Grignard reagent with *n*-hexyltrichlorosilane.[17] Crude monomer was purified by

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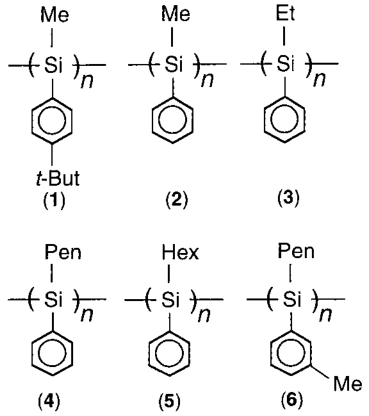
Table 1. Polymerization Results and Glass Transition Temperature (T_g) of PAAS Derivatives

polymer	M_w	M_w/M_n	T_g/K
1	3.2×10^5	2.2	355
2	6.2×10^5	2.4	343
3	4.2×10^5	2.1	333
4	3.2×10^5	2.6	343
5	2.8×10^5	2.0	268
6	2.6×10^5	2.2	323

Scheme 1. Molecular Structures of Poly(methyl-*p*-*tert*-butylphenylsilylene) (1), Poly(methylphenylsilylene) (2), Poly(ethylphenylsilylene) (3), Poly(*n*-hexylphenylsilylene) (4), Poly(*n*-pentylphenylsilylene) (5), and Poly(*n*-pentyl-(*m*-tolyl)silylene) (6)



distillation under reduced pressure. Dichloroethylphenylsilane and dichloromethylphenylsilane were obtained commercially. The other monomer data are as follows.

Dichloro-*n*-hexylphenylsilane; bp 140−145 °C/0.35 mmHg.^{13}C NMR (CDCl$_3$): δ 14.05, 20.01, 22.49, 22.54, 31.3, 32.1, 128.3, 131.5, 132.8, 133.3 ppm. ^{29}Si NMR: 19.28 ppm.

Dichloro-*n*-pentylphenylsilane; bp 125−130 °C/0.35 mmHg. ^{13}C NMR (CDCl$_3$): δ 14.55, 20.01, 22.79, 31.1, 32.0, 128.3, 131.5, 132.8, 133.3 ppm. ^{29}Si NMR: 19.20 ppm.

Dichloro-*n*-butylphenylsilane; bp 115−120 °C/0.35 mmHg. ^{13}C NMR (CDCl$_3$): δ 14.75, 20.21, 22.69, 30.30, 128.3, 131.5, 132.8, 133.3 ppm. ^{29}Si NMR: 19.52 ppm.

Dichloro-*n*-propylphenylsilane; bp 100−105 °C/0.35 mmHg. ^{13}C NMR (CDCl$_3$): δ 16.20, 17.15, 23.05, 131.5, 132.8, 133.3 ppm. ^{29}Si NMR: 19.02 ppm.

Dichloromethyl(*p*-*tert*-butylphenyl)silane; bp 130−135 °C/0.35 mmHg. ^{13}C NMR (CDCl$_3$): δ 16.75, 23.05, 128.3, 131.5, 132.8, 133.3 ppm. ^{29}Si NMR: 19.60 ppm.

Polymer Synthesis. Polymer **5** was typically polymerized by conventional Wurtz-type condensation as described below. We added 2.3 g (0.1 mol) of sodium dispersion and 10.4 g (0.04 mol) of dichloro-*n*-hexylphenylsilane dropwise in an argon atmosphere to a mixture of 100 mL of dry toluene. The mixture was stirred slowly at 130 °C for 2 h. The viscous purple mixture was diluted with toluene and filtered through a 0.45 μm Teflon filter. We isolated the high molecular weight fraction by centrifugation after fractional precipitation in a mixed 2-propanol−toluene solution and then dried it at 100 °C in vacuo overnight. We further purified all the polymer samples for optical spectral measurement by precipitating them from a toluene solution into a nonpolar solvent such as hexane. The molecular weights of the PAAS samples used in this work are listed in Table 1.

Results and Discussion

The chemical structures of the PAAS derivatives and their abbreviations are shown in Scheme 1. Here, we increased the chain length of the alkyl substituent progressively in a series of **2**−**5** in order to test the effect of steric bulk on the chain silicon, and we introduced *tert*-butyl and methyl groups at the para position of **1** and at the phenyl ring of **6**, respectively. The polymerization results of the PAAS derivatives are summarized in Table 1. Since the optical spectra of low molecular weight polysilylenes are very different from those with high molecular weights, we carefully isolated high molecular weight fractions greater than 10^5 g/mol from the bimodal molecular weight distributions. Nevertheless, no high molecular weight fractions were formed from poly(*n*-butylphenylsilylene) or poly(*n*-propylphenylsilylene). Because we only obtained low molecular weight fractions of less than 10^3 g/mol, we excluded these polymers from the discussion in this study. Table 1 also shows the glass transition temperature (T_g) determined by DSC analysis. PAAS has a relatively high T_g of above 250 K except for **5**.

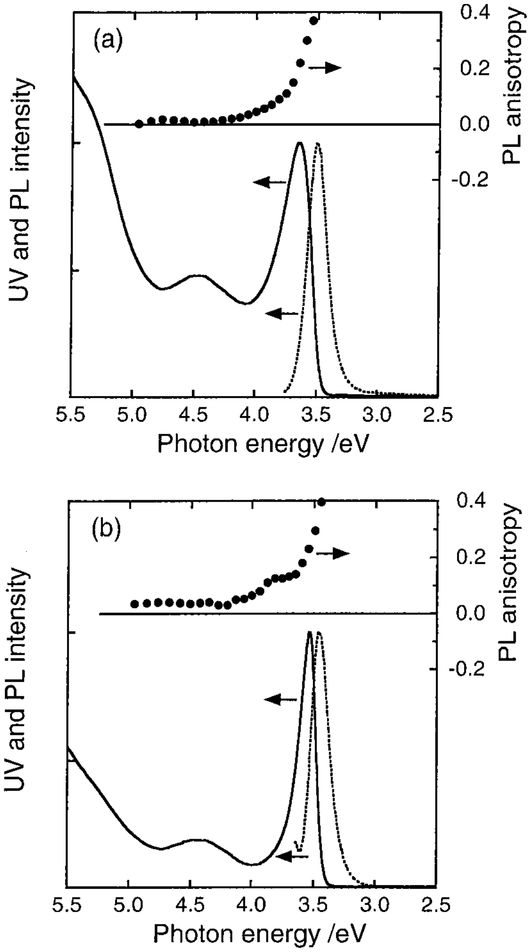


Figure 1. (a) UV absorption and PL spectra, normalized by the peak intensity, in arbitrary units, and PLA spectra of poly(methylphenylsilylene) (**2**). (b**)** UV absorption and PL spectra, normalized by the peak intensity, in arbitrary units, and PLA spectra of poly(*n*-pentylphenylsilylene) (**4**).

Figure 1 compares the UV absorption and PL spectra, normalized by the peak intensity and the PLA spectra of **2** and **4** THF at 296 K. The spectral profiles of **1** and **3** were similar to those of **2**, and the spectral profiles of **5** and **6** were similar to those of **4.** All exhibited a sharp absorption maximum around 3.5 eV with a broad weak absorption around 4.5 eV. We ascribe the former to the transition from the ground state to the lowest energy level of the exciton in the Si backbone, while the latter is due to the phenyl π−phenyl $\pi^{*\bullet}$ transition.[18,19] The full width at half-maximum (fwhm) and the 3.5 eV peak

Table 2. Fwhm and the 4.5 eV Peak Intensity Normalized by the Silicon Repeating Unit of the PAAS Derivatives

polymer	fwhm (eV)	peak intensity ((Si repeat unit)$^{-1}$ cm^{-1} dm^3)
1	0.48	7800
2	0.40	9800
3	0.40	9500
4	0.16	17000
5	0.16	17000
6	0.14	18000

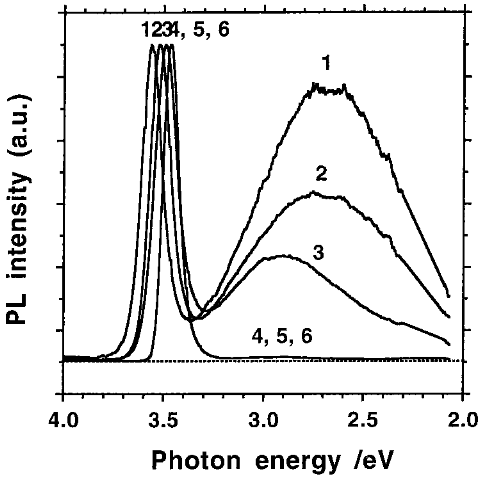


Figure 2. PL spectra, in arbitrary units, of (a) poly(methyl-*p*-*tert*-butylphenylsilylene), (b) poly(methylphenylsilylene), (c) poly(ethylphenylsilylene), (d) poly(*n*-pentylphenylsilylene), (e) poly(*n*-hexylphenylsilylene), and (f) poly(*n*-pentyl-*m*-tolylsilylene) in solid films at 20 K excited at 4.5 eV corresponding to the aromatic $\pi-\pi^*$ transition.

intensity normalized by the Si repeating unit of the PAAS derivatives are summarized in Table 2. The fwhm value of **4**, **5**, and **6** (group 2) is about half that of **1**, **2**, and **3** (group 1), and the peak intensity of group 2 is approximately twice that of group 1. The fhwm of **6** is the smallest and the peak intensity of **6** is the largest among the PAAS derivatives. The narrower absorption of group 2 at 3.5 eV suggests that the main chain has a more regular spatial conformation.[20]

Another significant difference between the spectral features of groups 1 and 2 is the shape of their 3.5 eV absorption and PL bands. There is a mirror-image relationship between the 3.5 eV absorption and PL bands of group 2, although not for those of group 1. The polysilylene absorption spectrum results from a convolution of various chromophore segments with different excitation energies. When segments with higher absorption energy are excited, the photoexcited electron−hole pair migrates into those segments with a lower energy absorption, from which the emission occurs.[21,22] Consequently, the mirror-image relationship suggests that the backbone conformation in group 2 has a more regular spatial conformation than that of group 1. Nevertheless, the PLA data of all the samples decreased monotonically from 0.35 to 0.05 when the excitation energy around 3.5 eV absorption changed from 3.5 to 4.0 eV, indicating conformational inhomogeneity and suggesting that the relative arrangements of the absorbing and emitting segments are not collinear.

Figure 2 compares the PL spectra of PAAS derivatives in the film at 20 K excited at 4.5 eV corresponding to the aromatic $\pi-\pi^*$ transition. (Here, the spectra are normalized at the peak intensities of the U−PL bands.) We observed almost no V-PL band from **4**, **5**, and **6**.

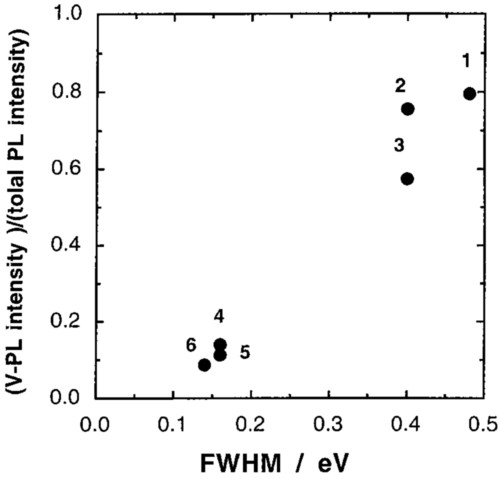


Figure 3. ^{29}Si NMR spectra of **1**, **2**, and **5**.

Three possible explanations have been considered for the origin of the V-PL from **2**: (1) the triplet-state model (TS) model,[23] (2) the Si σ-phenyl π^* (CT) model,[19,24] and (3) the backbone defect (BD) model.[11,25,26] We believe that the BD model is more appropriate for the origin of the V-PL for the following reasons.

(1) Previous studies[27] using several highly purified poly(dialkylsilylene)s have detected the triplet state of poly(methylpropylsilylene) as a narrow emission band with an fwhm of 0.04 eV, which is red-shifted by only ~0.17 eV relative to the corresponding fluorescence spectra. The V-PL band is broad and red-shifted by approximately 0.8 eV relative to the corresponding fluorescence spectra. Consequently, the TS model can be excluded as the origin of the V-PL from **2**.

(2) Although a theoretical calculation for idealized, stereoregular **2** predicts that the CT state is responsible for the V-PL, no concrete experimental evidence has yet been provided.

(3) A conventional Wurtz-type coupling reaction of dichlorosilane with alkali metal is often used to synthesize polysilylene derivatives. The polymers contain a small number of structural defects such as branching points. Our studies of ^{29}Si NMR and IR spectra based on a BD model of **2** suggest that a small quantity of silicon-based branching defects is incorporated in **2** in the polymerization process. This results in weak Si−Si bonding states and has a significant effect on the V-PL.[11] The BD model empirically predicts the absence of the V-PL at defect densities of less than 1%.

Figure 3 shows ^{29}Si NMR spectra of **1**, **2**, and **5** among groups 1 and 2. The ^{29}Si NMR spectra of poly(methyphenylsilylene) and poly(methyphenylsilylene) incorporating silicon-based structural defects have already been studied in detail.[11] The defects, which consist of an organosilyne unit and about three methylphenylsilylene units near the branch, are presumed to contain lengthened Si−Si bonds. The ^{29}Si NMR spectra of poly(methyphenylsilylene) show two broad signals around −35 and −45 ppm in the vicinity of the three sharp main signals due to stereochemical triad conformations. The two additional ^{29}Si NMR signals around −35 and −45 ppm have been identified as the above structural defects.[11] The ^{29}Si NMR spectra of our polymer **2** also exhibit two additional signals around −35 and −45 ppm resulting from structural defects, as shown in Figure 2. The intensity of the two additional signals of polymer **1** increased, compared with that of **2**. By contrast, the

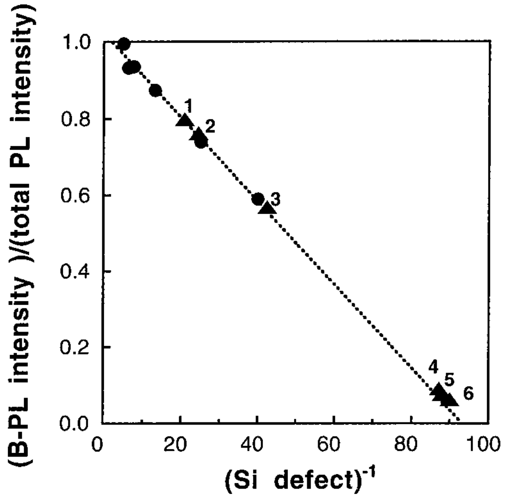


Figure 4. Relationship between the fwhm and the ratio of the integrated area intensity of the V-PL relative to total PL.

signals of **5**, originating from the structural defects, were barely detectable. We were unable to observe any ^{29}Si NMR signals originating from the structural defects of other polymers of group 2. By contrast, the V-PL intensity of group 1 increased when the structural defects increased. Thus, the ^{29}Si NMR data show that the number of structural defects has a great influence on the V-PL intensity.

Figure 4 shows the relationship between the absorption fwhm and the ratio of the integrated area of the V-PL to total fluorescence. As the value of fwhm decreases, the relative intensity of the V-PL band also decreases. This suggests that PAAS with a more regular spatial conformation has a relatively lower V-PL intensity. Compared with the less sterically hindered polymers of group 1, the overcrowded branched polymers of group 2 are more likely to decompose easily into low molecular weight fragments at the branching sites as a result of a thermal reaction. Therefore, even if such branching defects were incorporated in the silicon backbone, only nonbranched polymers of group 2 might be isolated as a high molecular weight fraction. To obtain high molecular weight PAAS derivatives that show no V-PL, the alkyl pendants should be pentyl or longer.

Figure 5 plots the relationship between the ratio of the integrated area of the V-PL and the structural defects. (Data for **2** are taken from ref 11.) The structural defects are estimated to amount to less than 1% in the group 2 polymers. There are fewer defects in group 2 than in group 1. Polysilylenes **4**, **5**, and **6** are expected to have a more spatially homogeneous conformation with fewer structural defects than group 1. Scheme 2 shows the molecular conformation proposed in this study. The conformation of group 1 is spatially inhomogeneous with branching defects, as shown in Scheme 2a. The conformation of group 2 is spatially homogeneous without branching defects, as shown in Scheme 2b. We assume that the number of structural defects can be estimated from the absorption and PL spectral features of PAAS. The mirror-image relationship between absorption and PL and the small fwhm (below 0.2 eV) also suggest that group 2 PAAS have a small number of structural defects.

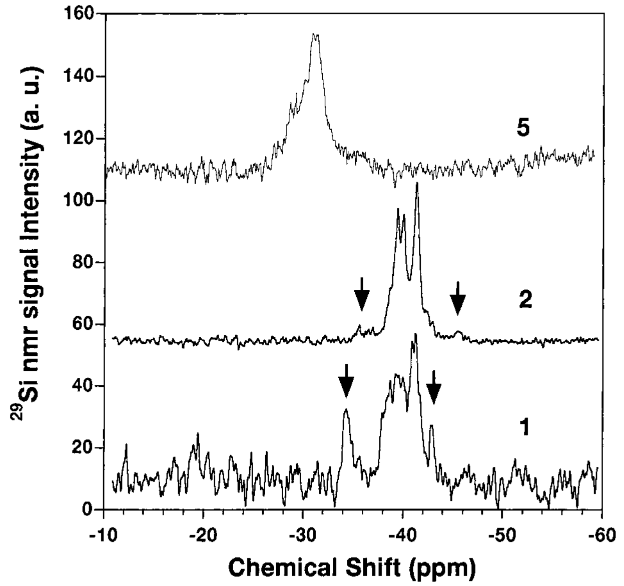
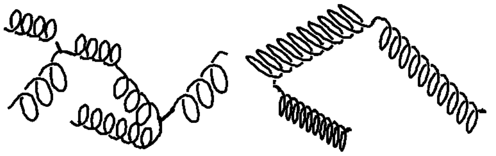


Figure 5. Relationship between the structural defects and the ratio of the integrated area intensity of the V-PL of the PAAS derivatives. This figure is reproduced from ref 11. The closed circles are taken from data obtained in ref 11, and the closed triangles are the data taken in this study. The number in the figure refers to the sample abbreviation used in the present paper.

Scheme 2. Schematic View of the Main Chain Conformation of Polymers of Poly(methyl-*p*-*tert*-butylphenylsilylene) (1), Poly(methylphenylsilylene) (2), Poly(ethylphenylsilylene) (3), Poly(*n*-pentylphenylsilylene) (4), Poly(*n*-hexylphenylsilylene) (5), and Poly(*n*-pentyl (*m*-tolyl)silylene) (6)



(a) PAPS conformation with branching defects, showing B-PL

(b) PAPS conformation without branching defects, showing no B-PL

Conclusions

We investigated the UV absorption, PL, and PL anisotropy spectra of a range of poly(alkylarylsilylene)s in solution at room temperature and in thin film in the 20−296 K range. Although we invariably found a V-PL band from **1**, **2**, and **3** in thin films, the V-PL band from **4**, **5**, and **6** is scarcely detectable in the room temperature to 20 K range. The ^{29}Si NMR spectral data were closely connected with the fact that the V-PL intensity increases with the increasing number of structural defects. We also ascribed the difference in the PL characteristics to the extended global shape with a spatially homogeneous local conformational structure in solution and in solid films. The mirror-image relationship between the absorption and PL and the small fwhm might be evidence that PAAS derivatives have very few structural defects. PAAS derivatives that are free of structural defects are promising as UV-light-emitting polymer materials with no visible emission over a wide temperature range.

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