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Preparation of Novel Photoluminescent Oligocarbosilanes by Hydrosilylation

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Introduction. Photoluminescent polymers have been of interest recently due to their potential application as light-emitting diodes (LEDs).[1,2] They offer flexibility in molecular design and good processability and are inexpensive relative to their inorganic counterparts. Furthermore, it is possible to tune their luminescent properties at the molecular level. Since the first report of poly(*p*-phenylenevinylene) (PPV)-based LEDs,[3] many PPV derivatives with improved solubility, processability, and quantum efficiency have been prepared.[4] Additionally, the incorporation of silicon into PPV side chains[5−7] and backbones has been reported.[8−10] Silicon-containing PPVs are attractive because of improved solubility and processability due to flexibility around the silicon atoms. Also, silicon atoms in the polymer backbone interrupt the regular π-conjugation, resulting in unusual optical properties.[8,11]

We have investigated the use of hydrosilylation to prepare silicon-containing PPV derivatives. Hydrosilylation has been employed in polymerizations since it was first used to polymerize vinyldimethylsilane.[12] While Pt-catalyzed hydrosilylation is traditionally performed with chloroplatinic acid, recently the 1,3-divinyltetramethyldisiloxane−Pt complex (Karstedt's catalyst) has been utilized.[13] Herein, we report a simple preparation of light-emitting oligocarbosilanes by hydrosilylation with Karstedt's catalyst. These oligomers are some of the first examples of photoluminescent poly(silylenevinylene)s with pendant phenyl groups.[14] They are unique in that they contain both conjugated and cross-conjugated segments.

Results and Discussion. Two compounds, (phenylethynyl)dimethylsilane[15] (**1**) and (phenylethynyl)methylphenylsilane[16] (**2**), were prepared by reaction of lithium phenylacetylide with dimethylchlorosilane or methylphenylchlorosilane, respectively (Scheme 1). Karstedt-catalyzed oligomerization of **1** or **2** was carried out in an argon atmosphere in a sealed pressure tube. The initially colorless monomer became dark brown within 1 min after addition of catalyst. Variable time and temperature studies of the reactions showed that conditions of 80 °C for 48 h minimized time to completion while maximizing chain length. Efforts to precipitate the oligomers from methanol were not successful. The catalyst was removed by flash column chromatography on silica gel, giving oligomers **1a**, M_w/M_n = 1300/1000, and **2a**, M_w/M_n = 1430/1320 (Scheme 1), that fluoresce in the UV region (Figures 1 and 2). ^{1}H NMR end group analysis corresponds reasonably well to the GPC data, giving M_n = 1100 and M_n = 1500 for **1a** and **2a**, respectively. The ^{1}H NMR integration ratio of aromatic, vinylic, and SiMe resonances equals the expected ratios in the oligomers. Both oligomers are glassy solids at room temperature, with **1a** being dark orange and **2a** being dark brown. They are freely soluble in common organic solvents and have not shown any degradation in ambient conditions as evidenced by ^{1}H and ^{13}C NMR. Oligomers **1a** and **2a** are stable to about 150 °C in a nitrogen atmosphere by TGA. At about 300 °C, catastrophic weight loss occurs until only 5% original mass remains by 500 °C.

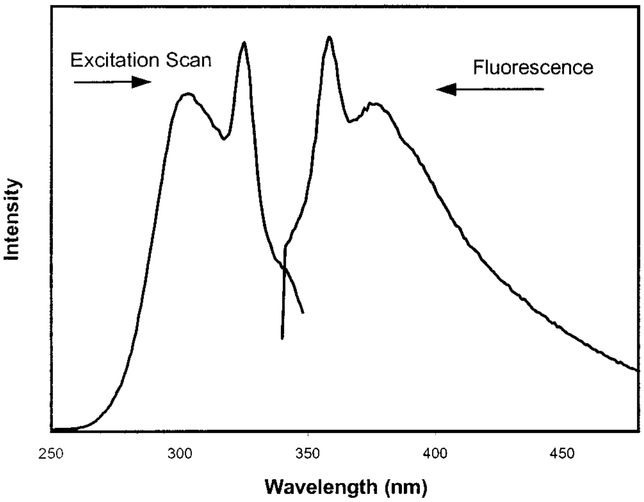


Figure 1. Excitation scan and fluorescence of **1a**.

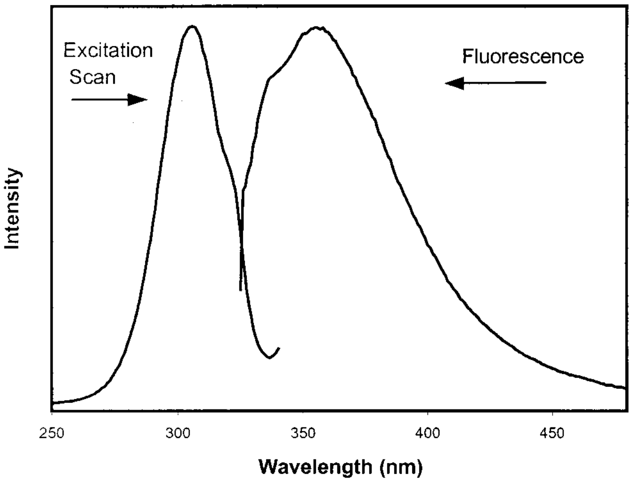
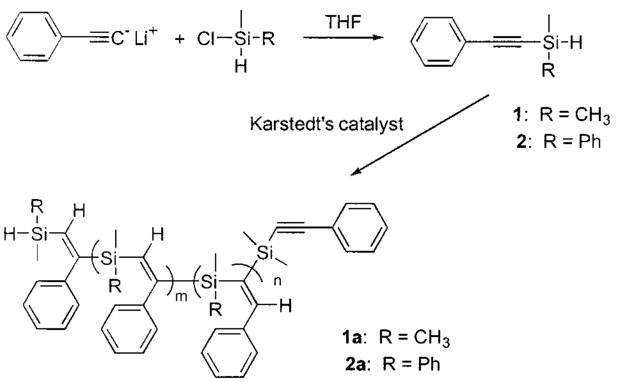


Figure 2. Excitation scan and fluorescence of **2a**.

Scheme 1. Synthesis and Oligomerization of 1 and 2



While Pt-catalyzed hydrosilylation proceeds stereospecifically by cis addition, it is not necessarily regiospecific.

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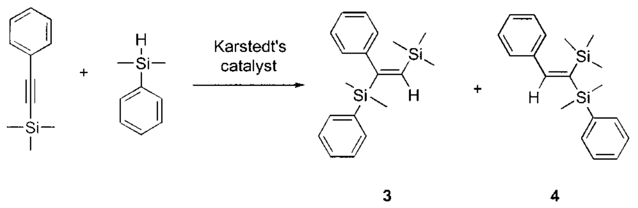
Scheme 2. Synthesis of Model Compounds 3 and 4



Oligomers **1a** and **2a** are unique in that they contain both conjugated and cross-conjugated segments, as a consequence of α- and β-addition. A Pt-catalyzed hydrosilylation reaction between (phenylethynyl)trimethylsilane and dimethylphenylsilane was carried out to produce monomeric models for the α- and β-addition processes which occur in the Pt-catalyzed oligomerizations (Scheme 2). Analysis of the reaction by ^{1}H and ^{13}C NMR, IR, and GC/MS and comparison with the literature[17] revealed 1-phenyldimethylsilyl-2-(trimethylsilyl)-phenylethene (**3**) as the major product (83%). Evidence for another product, 2-phenyldimethylsilyl-2-(trimethylsilyl)phenylethene (**4**) (14%), comes from the presence of additional signals in the aromatic and methyl regions of the ^{13}C NMR spectrum and from GC/MS. In accordance with the model reaction, Scheme 1 illustrates the two types of repeat units, *m* and *n*, within the oligomers. The *m*-type repeat units are a result of hydrosilylation occurring by β-addition and represent the majority of the units, whereas the *n*-type repeat units are cross-conjugated units formed by α-addition. Since overlapping vinylic hydrogen resonances in the *m*- and *n*-type units of the oligomers prohibit their distinction by ^{1}H NMR, further studies are necessary to confirm that the ratios of *m*- to *n*-type units in the oligomers parallel the results of the model reaction.

The fluorescence spectrum obtained for **3** differs significantly from that of the oligomers. When irradiated at 240 nm, **3** fluoresces weakly at 297 nm. When irradiated at 240 nm, **1a** fluoresces with maxima at 358 and 377 nm (Figure 1). When irradiated at 240 nm, **2a** fluoresces with a maximum at 355 nm (Figure 2). The longer wavelength fluorescence of **1a** and **2a** with respect to model compound **3** suggests that the fluorescence of the oligomers is not due to isolated styrene-type chromophores. The difference in emission wavelength may be due to the occurrence of conjugation through the silicon atoms in the oligomer backbones or to interchain aggregation of oligomer chains. Kim and Shim have prepared poly(phenylenevinylenesilylene)s having slightly greater molecular weights than **1a** and **2a** that fluoresce from 370 to 420 nm.[18] The comparatively shorter emission wavelengths of **1a** and **2a** are consistent with their shorter conjugated segments. We are currently investigating the concentration dependence of the emissions of the oligomer solutions to better understand the photophysics of the oligomers.

The infrared spectra of **1** and **2** show an intense absorbance at 2161 cm^{-1} due to the Si−H stretch. The signal due to the C−C triple bond stretch is likely masked by the broad Si−H absorbance. The IR spectra of **1a** and **2a** show a sharp, less intense absorbance at 2158 cm^{-1} due to Si−H end groups and a band at 2113 cm^{-1} due to C−C triple-bond end groups.

Preliminary studies in our group show that oligomerization of **1** using Wilkinson's catalyst, $Rh(PPh_3)_3Cl$, gives a variation of **1a** that fluoresces at 400 nm, consistent with a greater degree of conjugation in the oligomer backbone. Currently, we are working to analyze the microstructure of **1a** to attempt to understand why Rh catalysis produces a longer wavelength emitter than Pt catalysis.

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Supporting Information Available: Materials, instrumentation, and procedures for preparation and spectral data for **1**, **2**, **1a**, **2a**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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