

## Synthesis and Photophysical Studies of Silylene-Spaced Divinylarene Copolymers. Molecular Weight Dependent Fluorescence of Alternating Silylene–Divinylbenzene Copolymers

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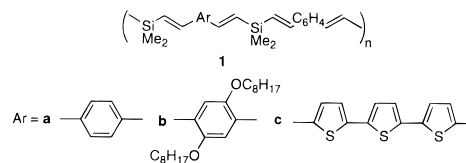
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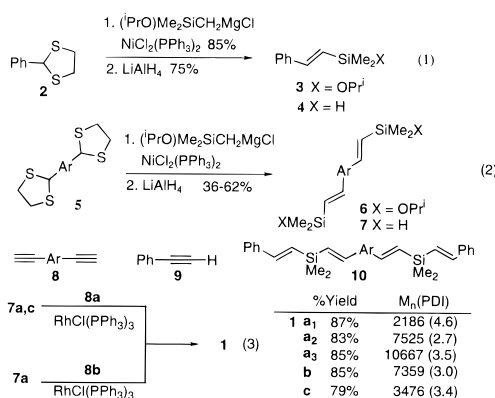
Received April 30, 1997

Introduction of spacers between well-defined chromophores in the polymeric chain can occasionally increase the processibility, and in the mean time, the emission wavelength can be predicted.<sup>1–7</sup> There has been an increasing use of tetrahedral silylene moiety as a bridge connecting chromophores in polymers.<sup>3–7</sup> Recent study indicates that a silylene spacer between two conjugated moieties facilitates the intramolecular photoinduced charge transfer process.<sup>8</sup> When the polymer contains a silicon linkage, it is envisaged that the polymer could be highly folded such that the two  $\pi$ -conjugated moieties may be located in close proximity and interaction between these chromophores may result in interesting photophysical behaviors.<sup>9</sup> Hydrosilylation, *inter alia*,<sup>5–7,10</sup> provides a useful entry for the synthesis of  $\sigma,\pi$ -conjugate organosilicon polymers.<sup>3,4,11,12</sup> However, owing to the accessibility of silane monomers,

syntheses are normally limited by using alkynyl silyl hydrides as starting materials. We recently developed a convenient procedure to prepare vinylsilanes from the corresponding aryl- or vinyl-substituted dithioacetals.<sup>13</sup> It was felt that conjugated silyl hydride precursors can be efficiently obtained by this method. In this paper, we report a convenient synthesis and the photophysical investigations of alternating silylene–divinylarene copolymers **1**.



Treatment of **2** with  $\text{Me}_2(\text{iPrO})\text{SiCH}_2\text{MgCl}$  in the presence of 5 mol % of  $\text{NiCl}_2(\text{PPh}_3)_2$  in refluxing benzene gave **3** in good yield. Reduction of the Si–O bond in **3** with LAH yielded **4** (eq 1).<sup>13</sup> Bissilylhydrides **7** were prepared similarly (eq 2). Treatment of **4** with **8b** in the presence of 0.5 mol % of  $\text{RhCl}(\text{PPh}_3)_3$  gave **10b** in 76% yield. Alternatively, **9** was allowed



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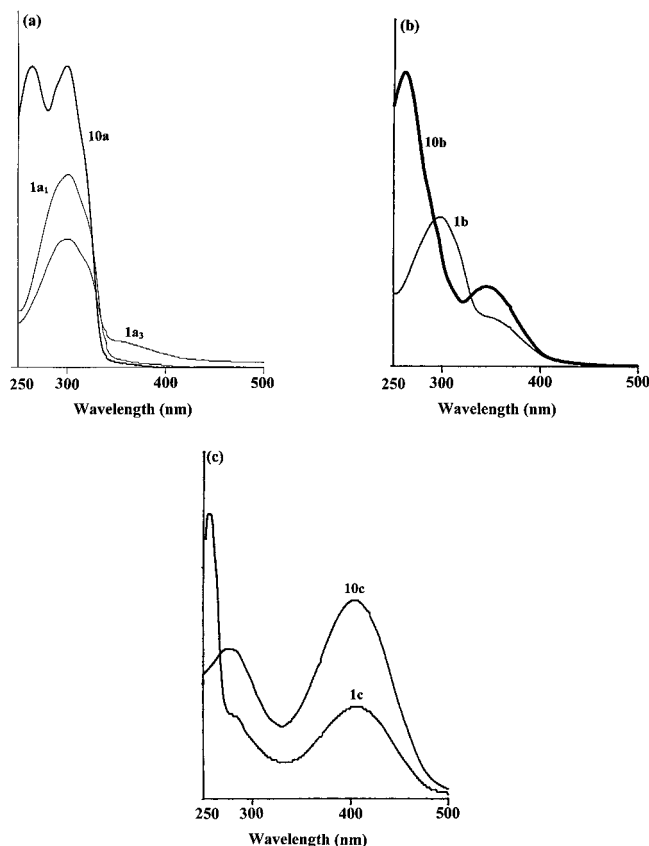
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to react with **7a,c** under the same conditions to afford the monomers **10a,c** in 85 and 78% yields, respectively. Monomers **10** were used as reference compounds for photophysical studies. In a similar manner, the rhodium-catalyzed hydrosilylation of **8** with **7** yielded polymers **1** (eq 3). It is noteworthy that the average molecular weight ( $M_n$ ) of **1** depends on the reaction conditions. Higher concentration and longer reaction times favor the formation of **1** with a higher molecular weight.

The absorption spectra for **1** and **10** are compared in Figure 1. No significant shifts between the polymers **1** and the corresponding monomer **10** were observed. However, there appeared a weak absorption in the region of 340–400 nm for **1a**, and the intensity slightly increases with the molecular weight of **1a** (Figure 1a).

Polymer **1a** exhibited dual fluorescence spectra (Figure 2a). The higher energy emission at ca. 340 and 360 nm for **1a** is compatible with those for **10a**. The relative intensity of the emission in the blue light region increases with the molecular weight of **1a**, and vibronic fine structures were observed in this region. The emission profiles remained essentially unchanged with concentration (5–100-fold) and with solvents (<8 nm, in MeCy, benzene, or  $\text{CHCl}_3$ ). Time-resolved fluorescence spectra of **1a<sub>3</sub>** and **10a** in  $\text{CHCl}_3$  were monitored at 341 and 414 nm. The fluorescence of **1a<sub>3</sub>** at 414 nm showed a slow decay with  $\tau = 1.1$  ns. On the other hand, both **1a<sub>3</sub>** and **10a** exhibited a fast fluorescence decay ( $\tau \approx 120$  ps) at 341 nm. An additional slow decay for **10a** was also observed at 341 nm, and its lifetime

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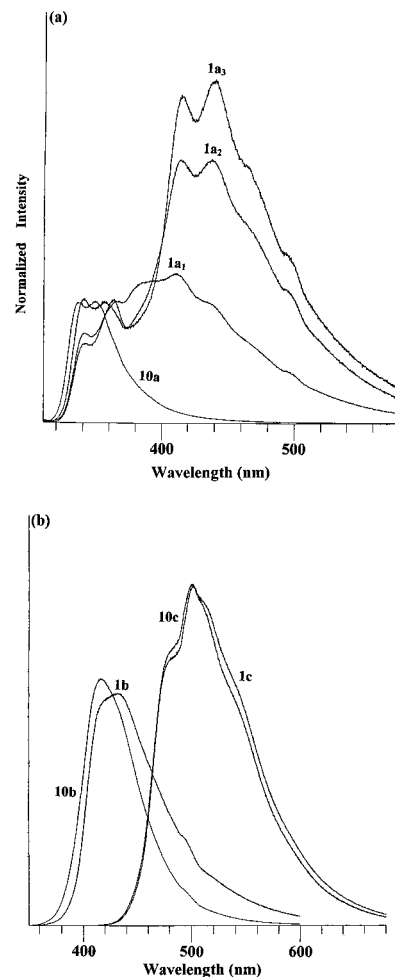
**Figure 1.** Absorption spectra for (a) **1a** and **10a**, (b) **1b** and **10b**, and (c) **1c** and **10c**.

was compatible with that fitted for the decay at 414 nm. When the fluorescence spectrum of **1a<sub>3</sub>** was monitored at 1 ns delay time after laser excitation, only low-energy emission was observed (see the Supporting Information). These data indicated that the emission of **1a** at these two wavelengths may be arising from different species.

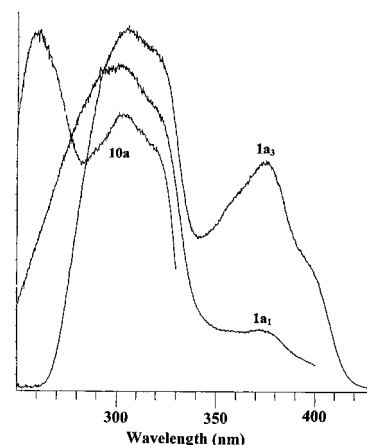
In the excitation spectra for **1a** (Figure 3), the intensity at 375 nm increases with the molecular weight, and such enhancement is substantial in comparison with those in the absorption spectra. These observations suggested that significant intramolecular interactions between lumophores in **1a** both at the ground and at the excited states might occur, and this interaction seemed to be more important as the polymer becomes larger. It is noteworthy that intrachain aggregation of chromophores has also been observed in the block copolymers obtained by ring-opening metathesis polymerization (ROMP) of [2,2]paracyclophane and norbornene.<sup>9a</sup> AM1 and Hartree-Fock (3-21G\*) calculations on divinyl- and distyrylsilanes suggested that the molecules are quite flexible. Accordingly, the opportunity for one chromophore unit in **1a** located proximal to the other in space would increase with the molecular weight.

In contrast to the emission properties of **1a**, there was not much difference in the fluorescence spectra between polymers **1b,c** and the corresponding monomers **10b,c** (Figure 2b). This implies that the above-mentioned intramolecular interaction may not exist in these polymers. These polymers contain either the bulky alkoxy moiety in **1b** or ter-aryl unit in **1c** as part of the backbone. The steric hindrance of the alkoxy group and the rigidity of the ter-aryl moiety might prohibit the chromophores in these polymers in close proximity. It is interesting to note that the emission frequencies of the alkoxy-substituted **1b** also fall within the blue light region (Figure 2b).

In summary, we have demonstrated that a new versatile approach toward the synthesis of a variety of co-silylene-conjugated polymers. The photophysical studies have shown



**Figure 2.** Emission spectra for (a) **1a** of different molecular weights and **10a** and (b) **1b,c** and **10b,c**.



**Figure 3.** Excitation spectra for **1a** at different molecular weights and **10a**.

that significant intramolecular interaction between lumophores occurs in **1a**. Our system involving a simple divinylarene moiety in these silylene-spaced copolymers could result in the emission to occur in the blue light region.

**Acknowledgment.** This work was supported by the National Science Council of the Republic of China.

**Supporting Information Available:** Spectral data and experimental procedures for synthesis and spectrophotometric measurements of **1** and **10**, Hartree-Fock (3-21G\*) calculations on divinylsilanes, and time-resolved fluorescence spectra of **1a<sub>3</sub>** and **10a** (9 pages). See any current masthead page for ordering and Internet access instructions.