

## Communications to the Editor

### An Abrupt Solvatochromic Transition in a Polar Polysilane

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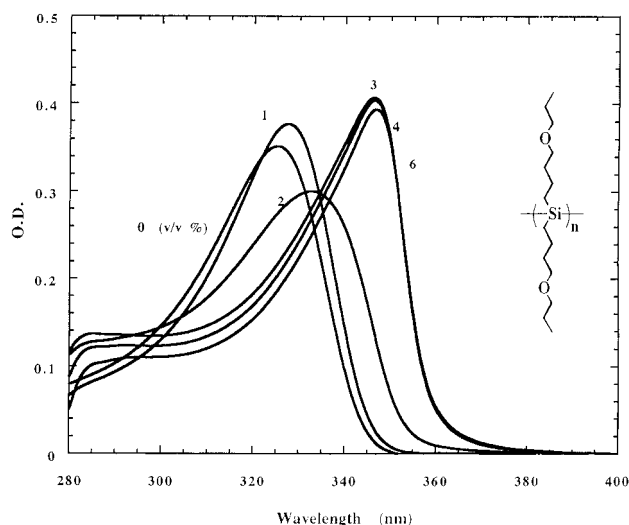
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We have observed a sudden solvatochromic transition in benzene or chloroform solutions of the polymer poly[bis(4-propoxybutyl)silylene] (PPBS). The absorption band at 325 nm in the UV spectrum of PPBS is replaced by an absorption at 348 nm when small amounts of 1,1,1,3,3,3-hexafluoro-2-propanol are added. This unprecedented behavior may result from hydrogen bonding of the fluoroalcohol to the oxygen atom in the polymer side chains, inducing an abrupt conformational transition.

Polysilane polymers display strong electronic absorption bands in the near-ultraviolet region, assigned to  $\sigma \rightarrow \sigma^*$  transitions.<sup>1</sup> Many polysilanes exhibit marked thermochromism of this UV absorption, resulting from temperature-dependent changes in the polymer conformation that alter the  $\sigma$ -conjugation.<sup>2</sup> Other types of chromotropic behavior are less common for polysilanes, although electrochromism<sup>3</sup> and piezochromism<sup>4</sup> have been reported for isolated examples. Solvatochromism, the dependence of the absorption spectrum upon the nature of the solvent, is known for  $\pi$ -conjugated polymers in the polyacetylene<sup>5</sup> and polythiophene<sup>6</sup> families, but among polysilanes solvatochromism has been reported only for poly[bis(*p*-alkoxyphenyl)silenes],<sup>7</sup> which have two absorption maxima, the longer-wavelength band becoming more intense in polar solvents.

Recently we have synthesized several polysilanes that have one or more oxygen atoms in alkyl side chains.<sup>8,9</sup> Unlike typical polysilanes, many of these oxygen-containing polymers display some kind of solvatochromic behavior. Here we describe the unusual properties of one example, poly[bis(4-propoxybutyl)silylene] (PPBS). The absorption maximum for PPBS



**Figure 1.** Ultraviolet spectra of PPBS in benzene, showing solvatochromic transition upon addition of  $(\text{CF}_3)_2\text{CHOH}$ . The numbers indicate the percent (v/v) of  $(\text{CF}_3)_2\text{CHOH}$  in benzene.

falls at 325 nm ( $\pm 1$  nm) in dilute solution in benzene, chloroform, or THF. Thus there is no solvatochromism of the usual sort, dependent on solvent polarity. However, PPBS exhibits a strong and unexpected solvatochromic change induced by hexafluoro-2-propanol.

As shown in Figure 1, when  $(\text{CF}_3)_2\text{CHOH}$  was added incrementally to a PPBS solution in benzene at 10 °C, a gradual shift to a slightly longer wavelength was initially observed. At a concentration of  $(\text{CF}_3)_2\text{CHOH}$  between 1 and 3% (v/v), an abrupt spectral transition to 348 nm was seen, with disappearance of the band near 325 nm. At the approximate midpoint of the transition, with 2%  $(\text{CF}_3)_2\text{CHOH}$  present, the intensity of the absorption band was somewhat reduced.

This is unusual, since the long-wavelength thermochromic transition of polysilanes is normally accompanied by a narrowing of the absorption band resulting in higher absorbance at  $\lambda_{\text{max}}$ . A similar unexpected decrease in absorbance upon solvatochromic transition has been observed for a polythiophene and attributed to partial precipitation; this may also explain the decreased absorption for PPBS.

To examine this possibility, PPBS was studied in a better solvent, chloroform, at 10 °C. Addition of  $(\text{CF}_3)_2\text{CHOH}$  led again to an abrupt solvatochromic transition (Figure 2), this time accompanied by band narrowing and intensification of the absorption. The critical concentration in  $\text{CHCl}_3$  was between 4 and 5% (v/v). This concentration is higher than that in benzene ( $\sim 2\%$ ) at the same temperature, suggesting that the interaction between the fluoroalcohol and the polysilane is partially inhibited in this more polar solvent. The solvatochromic transition is fully reversible; dilution with chloroform to reduce the  $(\text{CF}_3)_2\text{CHOH}$  concentration led to disappearance of the 348-nm band and reappearance of the 325-nm absorption.

$(\text{CF}_3)_2\text{CHOH}$  is known to be a uniquely powerful proton donor in hydrogen-bond formation,<sup>10</sup> and we propose that the solvatochromism of PPBS results from hydrogen bonding of  $(\text{CF}_3)_2\text{CHOH}$  to the oxygen atom of the side groups, inducing a conformational change to a more extended, trans-like arrangement of the polysilane chain.  $(\text{CF}_3)_2\text{CHOH}$  forms a strong

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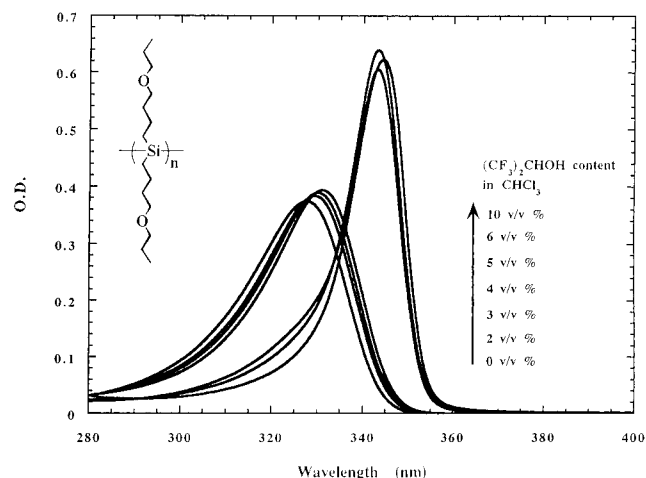
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**Figure 2.** Solvatochromic behavior of PPBS in  $\text{CHCl}_3$  upon addition of  $(\text{CF}_3)_2\text{CHOH}$ . The critical value for the solvatochromic transition is between 4 and 5% of  $(\text{CF}_3)_2\text{CHOH}$  (v/v).

hydrogen-bonded complex with THF,<sup>11</sup> and when PPBS dissolved in THF was treated with  $(\text{CF}_3)_2\text{CHOH}$ , no solvatochromism was observed, even at high (~20%) fluoroalcohol concentrations. The THF, we believe, competes for the fluoroalcohol hydrogen bonds, preventing the interaction with the propoxybutyl oxygens.

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Alcohols that are weaker hydrogen bond donors than  $(\text{CF}_3)_2\text{CHOH}$  do not induce solvatochromism. Thus 2-propanol causes no solvatochromic shift of PPBS in benzene, up to 20% (v/v) concentration. Acetic acid, 2-fluoroethanol, 2,2,2-trichloroethanol, and 2,2,2-trifluoroethanol, although they are all good proton donors in hydrogen bond formation,<sup>10</sup> likewise do not cause an abrupt solvatochromic shift; they produce only slight and gradual red shifting of the polysilane  $\sigma \rightarrow \sigma^*$  transition. Moreover, addition of  $(\text{CF}_3)_2\text{CHOH}$  to solutions of polysilanes lacking oxygen atoms, such as poly(di-*n*-hexylsilylene), causes no solvatochromic change.

PPBS, like many other polysilanes,<sup>1</sup> undergoes a thermo-chromic transition in which the 325-nm band disappears and is replaced by an absorption at 351 nm. The midpoint of the thermo-chromic transition is  $-45^\circ\text{C}$  in THF solution and  $-15^\circ\text{C}$  in the solid state; the latter temperature corresponds to an endotherm in the DSC trace. The solvatochromism of PPBS with  $(\text{CF}_3)_2\text{CHOH}$  also shows some dependence on temperature. For example, the critical concentration of  $(\text{CF}_3)_2\text{CHOH}$  to induce the solvatochromic shift in benzene is about 2% at  $10^\circ\text{C}$ , but increases to 5% at  $17^\circ\text{C}$ . Thus, one way of viewing the effect of  $(\text{CF}_3)_2\text{CHOH}$  on PPBS is that it greatly increases the temperature of the coil-to-rod-like, thermo-chromic transition.

The solvatochromic behavior of other oxygen-containing polysilanes is being investigated and will be reported elsewhere.

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