Ionochromism and Increase in Fluorescence Quantum Yield of an Ether-Substituted Polysilylene upon Adding Lithium Ions in Solution

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Introduction. Polysilylenes show intense absorption and fluorescence bands in the ultraviolet region, ascribed to electronic transitions involving extensively delocalized σ-electrons along the Si backbone.[1] In many polysilylenes the electronic absorption is thermochromic,[2,3] reflecting temperature-dependent changes in the conformation of the main polymer chain. In special cases other kinds of chromotropic behavior have been observed, including electrochromism,[4] piezochromism,[5] and solvatochromism.[6,7] Recently, solid films of polysilylenes containing ethyenedioxy units in the side chains have been shown to display ionochromism.[8] Upon addition of lithium salts, the thermochromic frequency shift for such polymers may either be inhibited (negative ionochromism) or accelerated (positive ionochromism).[9] Here, we report positive ionochromic behavior of a polysilylene *in solution*, affecting both the absorption and fluorescence spectrum.

Experimental Section. A. Synthesis. Sodium 2-ethoxyethoxide (165 g) in toluene (100 mL) was slowly added to 1,5-dichloroethane (254 g) at 5 °C. 1-Chloro-5-(2-ethoxyethoxy)pentane was isolated by distilling the reaction mixture under vacuum. ^{13}C NMR in $CDCl_3$: 14.28, 23.38, 28.91, 32.08, 44.91, 66.80, 68.20, 69.81, 70.25.

The chloride (50 g) was reacted with magnesium (3 g) at 75 °C. The mixture was added slowly to tetrachlorosilane (18 g) in dry diethyl ether at 40 °C. Di-6,9-dioxaundecyldichrolosilane (**1**) was isolated by distilling the reaction mixture in a vacuum. ^{13}C NMR in $CDCl_3$: 15.10, 24.38, 29.91, 32.88, 45.91, 67.90, 68.80, 70.51, 71.25. ^{29}Si NMR in $CDCl_3$: 32.08.

The monomer **1** (3 g) was reacted with sodium metal (0.5 g) in toluene (30 mL) for 30 min at 110 °C. After removal of toluene from the mixture in a vacuum, the resulting solids were dissolved in ethanol (100 mL) and filtered under an Ar gas pressure. A small amount of water was added to the filtrate, and the precipitate was isolated using a centrifuge apparatus. After drying the polymer at 100 °C overnight under reduced pressure, the purified poly[bis(ethoxyethoxypentyl)silylene] (PEEPS) was obtained as a white solid. The weight-average molecular weight of the polymer (M_w) was 2.2 $\times 10^6$, and the polydispersity index was 2.5, based on a calibration with polystyrene standards.

B. Spectroscopy. UV absorption and fluorescence spectra were measured with band-pass of 1 nm. The fluorescence quantum yield (Q-FL) was determined using quinine sulfate as a standard.

Results and Discussion. Figure 1 shows the absorption spectra of PEEPS in dilute di-*n*-butyl ether at 23 °C when lithium trifluoromethanesulfonate (LiTFMS) solution was added incrementally to the solution. At a LiTFMS:Si ratio of 200 (in moles), the absorption band was slightly red-shifted. Little further change took place up to a LiTFMS:Si molar ratio of 800; but when the ratio was increased to 1000, an abrupt shift of the absorption band from 325 to 350 nm occurred, along with significant band narrowing. The bathochromic shift suggests the formation of a more extended (transoid) conformation for the polysilylene chain,[1−3] and the narrowing of the band is consistent with an increase in the segment length.[10] We consider that the ionochromism results from a noncovalent interaction between the Li^+ cations of the LiTFMS and the oxygen atoms of the substituents, which induces a conformational change in the polymer to a more extended, transoid arrangement.

The samples containing LiTFMS also showed absorption at short wavelengths, <280 nm, which may be due to light scattering by aggregates of PEEPS with Li^+. Filtration of the solutions containing high concentrations of LiTFMS through a 0.45 μm filter removed all of the polymer from the solution, confirming that aggregation had taken place.

The fluorescence spectra of PEEPS as a function of LiTFMS concentration are shown in Figure 2. At a LiTFMS:Si molar ratio of 200, the fluoresence band was red-shifted from 344 to 354 nm. Little further change took place up to a LiTFMS:Si ratio in moles of 800. When the ratio was increased to 1000, the fluorescence band shifted abruptly from 354 to 359 nm. The Si unit concentration was 7.14×10^{-6} M at a LiTFMS:Si molar ratio of 1000. The full width at half-maximum of the fluorescence spectrum was 21 nm for the pure polymer, 17 nm at a LiTFMS:Si molar ratio of 200, and 14 nm at a LiTFMS:Si ratio of 2000. Thus, the spectral change of the fluorescence bands upon adding the salt was somewhat different from that of the absorption bands.

When a solution of PEEPS containing lithium salt at a LiTFMS:Si molar ratio of 1000:1 was diluted with solvent, the UV absorption spectrum was unchanged; no band at 325 nm for uncomplexed polymer was observed. When more polymer was added to a solution at the same 1000:1 LiTFMS:Si molar ratio, two bands at 325 and 350 nm were observed, without any weakening of the 350 nm band. These results indicate that the complexation is irreversible, at least at room temperature.

The polysilylene absorption spectrum results from a convolution of various segmented chromophores with different excitation energy.[11] When segments with higher energy absorption are excited, the photoexcited electron−hole pair migrates into segments with lower excitation energy, from which the emission occurs. The fluorescence spectra for polysilylenes strongly depends on emission from these segments with lower energy

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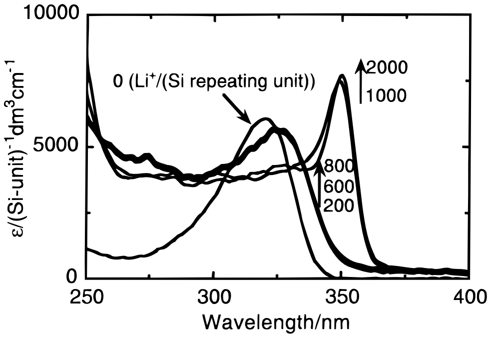

Figure 1. Absorption spectra of PEEPS in di-*n*-butyl ether at 23 °C. The numbers indicate the molar ratio of LiTFMS to the Si repeating unit of PEEPS.

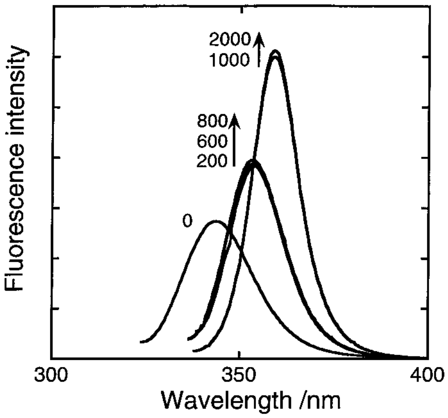

Figure 2. Fluorescence spectra, in arbitrary units, of PEEPS in di-*n*-butyl ether at 23 °C. The numbers indicate the molar ratio of LiTFMS to the Si repeating unit of PEEPS.

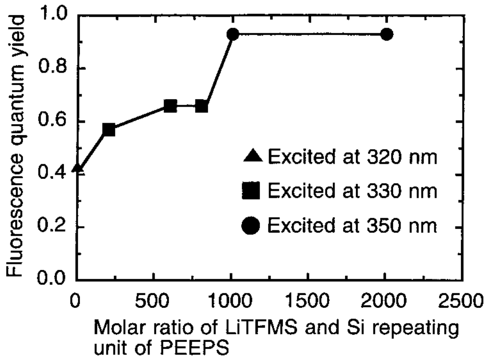

Figure 3. Lithium ion concentration dependence of quantum yield of PEEPS in di-*n*-butyl ether at 23 °C.

absorption. The bathochromic shift and narrowing of the fluorescence spectra observed for PEEPS at a LiTFMS: Si molar ratio of 200−800 suggest that even at this lithium ion concentration, the polysilane chain includes regions of more extended conformation, although this is difficult to detect from the absorption spectra.

Figure 3 shows the LiTFMS concentration dependence of the Q-FL at 23 °C. At the same concentration of LiTFMS that led to the ionochromic shift, the Q-FL value increased sharply, reaching a value of 0.93. To our knowledge, this is the highest reported Q-FL value for a polysilylene. We believe that both the formation of the extended conformation and the interaction between the LiTFMS and polysilylene substituents enhance the Q-FL value by increasing the conjugation length. These results may indicate a new way to improve the properties of polysilylenes in applications such as electroluminescencent devices,[12] where the fluorescence quantum efficiency is very important.

We have recently reported the optical properties of optically active poly[{6,9,12-trioxatetradecyl-(*S*)-2-methylbutyl}silylene] (PTMS).[13] The addition of LiTFMS to a PTMS solution in methanol, ethanol, *n*-butanol, di-*n*-butyl ether, or THF did not result in any ionochromic behavior. PTMS also does not show any significant thermochromism, exhibiting only a gradual blue shift as the temperature decreases. The main-chain conformation of PTMS may be fixed by the steric hindrance of the 6,9,12-trioxatetradecyl and (*S*)-2-methylbutyl substituent groups, so that temperature changes and noncovalent interactions between the LiTFMS and the oxygen substituents do not induce changes in the rigid main-chain conformation. In contrast, we observed significant thermochomism with PEEPS in ethanol. The 320 nm absorption peak red-shifted to 350 nm around −30 °C.

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