Phosphorescence from the Delocalized Triplet State of Polysilylenes

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Received: February 1, 1993

Fairly sharp phosphorescence is observed at 4.2 K for several polysilylenes synthesized by an anion polymerization method. No broad phosphorescence was observed in the spectral region where the phosphorescence was previously reported to exist. The small bandwidth and the small fluorescence–phosphorescence energy separation are in accord with our previous idea that the phosphorescence is from the delocalized triplet state of the polymers. The temperature dependence of the phosphorescence intensity is interpreted by a model in which a quenching level exists $\sim$60 cm^{-1} above the emitting level.

Introduction

Previous reports on the phosphorescence of polysilylenes have been controversial in both the spectral location and the nature of the emitting state. Three representative spectra reported so far for poly(methylpropylsilylene) are compared in Figure 1. Harrah and Zeigler[1] observed broad and somewhat structured long-lived luminescence for several polysilylenes inclusive of poly-(methylpropylsilylene) (Figure 1a). They claimed that the structures could be interpreted in terms of known vibrational energies, and they assigned the band to the phosphorescence of the polymer. Michl et al.,[2] on the other hand, observed broad and structureless long-lived luminescence (Figure 1b), and they ascribed the band to the phosphorescence. Even though the spectra observed by these two sets of authors for the same polysilylene are not identical in spectral location and structure, the spectra are more or less similar in a sense that the band is fairly broad (half width $\sim$4500 cm^{-1}). This broad feature is in sharp contrast to the well-studied sharp (half width $\sim$400 cm^{-1}) fluorescence[3] that has been attributed to the emission from the delocalized $^1(\sigma,\sigma^*)$ excited state. Because of the broadness of the band, both Harrah and Zeigler[1] and Michl et al.[2] ascribed the luminescence to the emission from the localized triplet excited state.

In contrast to these observations, we observed[4] fairly sharp phosphorescence of poly(methylpropylsilylene) at 4.2 K in much shorter wavelength region (Figure 1c). The spectral shape and bandwidth are both quite analogous to the fluorescence. Our assignment of the luminescence as the phosphorescence was further confirmed[4] by the decay analysis and the ODMR measurements.[5] Even though the analysis quite conclusively substantiates the triplet nature of the emitting state, there still remain several questions. First, there has been a supposition that the phosphorescence might come from both the localized and delocalized excited states. If this is true, both the sharp and the broad luminescence bands should be considered authentic. In this case we, first of all, should seek the source of the difference between the two reports[1,2] and further clarify the nature of the emitting level. We were previously[4] not able either to support or to negate this supposition because of the presence of an impurity band in the spectrum. In our previous spectrum shown in Figure 1c, a luminescence existed in the 380–450-nm region, and we ascribed the band to an impurity. (We ascribed this long-wavelength emission to an impurity because, first of all, the excitation spectrum is entirely different from the absorption spectrum, and further, the band is nonexisting in the ODMR action spectrum. In this sense, the long-wavelength band shown in Figure 1c differs from the somewhat analogous spectrum
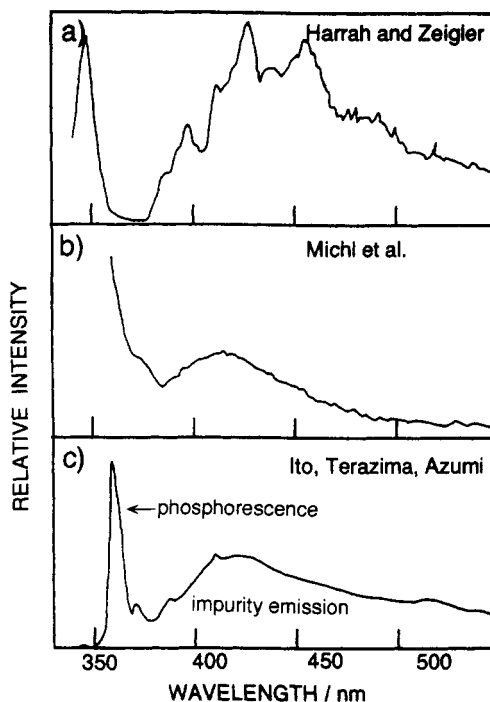
Figure 1. Previously reported phosphorescence of (SiMePr)$_n$: (a) Harrah and Zeigler, ref 1 of the text; (b) Michl et al., ref 2 of the text; (c) Ito et al., ref 4 of the text.

observed by Wilson and Weidman[7] and by Fujiki.[8]) The location of this impurity band almost overlaps with the luminescence observed by Harrah and Zeigler and by Michl et al. Our effort to remove the impurity by purification was unsuccessful. Incidentally, the polymer was synthesized by the Kipping method[9] and was purified by the freeze-dry method.[10] Due to the existence of the impurity emission, we were not certain whether or not the broad phosphorescence of the type reported previously[1,2] was hidden under this impurity band. The second question concerns the thermal quenching of the phosphorescence. That is, we ask why the phosphorescence is observed only at temperatures as low as 4.2 K. As for the third question, we consider whether the observation of the sharp phosphorescence can be generalized to other polysilylenes. In the present paper, we endeavor to answer these questions.

Our efforts along these lines have been realized by the recent development of a new method of synthesis of polysilylenes by Sakurai et al.[11] Since the polysilylenes synthesized by the new method, anionic polymerization of masked disilenes, appear to be less contaminated by impurities we have undertaken the phosphorescence measurements for several polysilylenes. The polysilylenes we have investigated are poly(methylpropylsilylene)
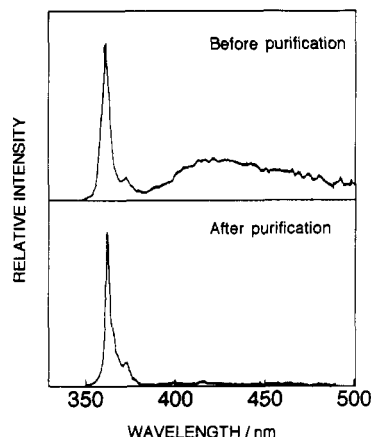
Figure 2. Phosphorescence of (SiMePr)$_n$ synthesized by anion polymerization observed at 4.2 K in benzene solution (a) without purification and (b) with purification.

[abbreviated hereafter as (SiMePr)$_n$], poly(butyltrimethyldisilanylene) [abbreviated hereafter as (SiMeBuSiMe$_2$)$_n$], and poly-(dimethyldihexyldisilanylene) [abbreviated hereafter as (SiMe$_2$-SiHex$_2$)$_n$].

Experimental Section

Polymerization of polysilylenes was carried out in a 50-mL two-necked flask, equipped with a magnetic stirrer, a rubber septum, and a three-way stopcock under dry argon. A solution of a monomer in THF, freshly distilled from sodium, was placed in the flask. A hexane solution of n-BuLi was added to the solution at −78 °C. The color of the solution changed to red immediately. The mixture was kept stirring for 30 min after removing the cooling bath. A few drops of ethanol were added to the mixture. Polymers were purified by removal of the solvent, precipitation, and further cycles of dissolving–precipitating followed by freeze-drying. (SiMe$_2$SiHex$_2$)$_n$: white solid; M_n = 6.1 × 10^4, M_w = 7.8 × 10^4, M_w/M_n = 1.3 (GPC, polystyrene standard). (SiMePr)$_n$: white solid; M_n = 1.81 × 10^4, M_w = 2.3 × 10^4, M_w/M_n = 1.3 (GPC, polystyrene standard). (SiMeBuSiMe$_2$)$_n$: translucent solid; M_n = 1.1 × 10^5, M_w = 1.7 × 10^5, M_w/M_n = 1.6 (GPC polystyrene standard).

Even though the polysilylenes were kept in the dark, the luminescence exhibited an impurity emission. The impurity emission, however, could be removed by reprecipitation from methanol solution. The success of the purification is in contrast to our previous experience in which the polysilylenes synthesized by the Kipping method could not be purified in a satisfactory manner.

The phosphorescence was measured for benzene solutions (the concentration was ~10^{-4} M monomer repeat). All sample preparation procedures were carried out under yellow light, since the polysilylenes are easily decomposed by light from a fluorescent lamp.

Phosphorescence was measured with a conventional phosphoroscope (dead time of ca. 1 ms) by a Spex 1702 monochromator equipped with a Hamamatsu R 1477 photomultiplier tube. Excitation was carried out by a 500-W Xe lamp. In order to avoid decomposition of the polymers, we tried to work with as low exciting light intensity as possible.

Results and Discussion

Effect of Purification. Phosphorescence spectra measured at 4.2 K for (SiMePr)$_n$ without and with purification are shown in Figure 2. The spectra for the other polymers are more or less similar. The spectrum of unpurified polysilylene has a broad and structureless band in the 400–500-nm region, somewhat analogous to the spectra reported previously.[1,2] This band was, however, nonexistent in the spectrum of purified samples. Therefore, the

broad long-wavelength band observed for crude materials is due to an impurity, at least in the present samples. It is very important to note that the band observed by Harrah and Zeigler[1] and by Michl et al.[2] was not observed in our purified polysilylenes. However, an impurity is not the sole origin of the broad visible band in the emission spectra of polysilylenes. A recent work by Wilson and Weidman[7] has demonstrated that the 340-nm σ–σ* emission band of linear poly(hexylmethylsilylene) is accompanied by a broad visible band possessing nonexponential decay behavior when 1–2% branching exists. They have suggested that incidental branching may be responsible for the presence of similar emission bands often observed for reportedly linear polysilylenes. It is thus concluded that our samples of polysilylenes are free from both impurities and branching.

Fluorescence and Phosphorescence. Fluorescence and phosphorescence spectra observed for the three purified polysilylenes are shown in Figure 3. For all compounds the phosphorescence is as sharp as the fluorescence. Vibrational structures associated with the fluorescence and the phosphorescence are similar but not identical; this subject will be discussed in another publication.[12]

The fact that nearly the same phosphorescence was observed for all three polysilylenes may well indicate that the observed phosphorescence spectra are all genuine. Because of the small bandwidth observed generally, we conclude that our previous assertion that the phosphorescence is from the delocalized $^3(\sigma,\sigma^*)$ state is justified for all polysilylenes in general.

The peak positions of fluorescence and phosphorescence and their energy differences are summarized in Table I. Both fluorescence and phosphorescence are shifted to the red as the length of the side chain increases, in agreement with several previous reports.[13,14] The singlet–triplet energy gap is ~1300 cm^{-1} for any polysilylene. The observed energy separation is almost in accord with the theoretical value of 2000 cm^{-1} calculated by Takeda[15] by a modified Hartree–Fock method for a completely delocalized system. The small energy gap is also in accord with the delocalized nature of the excited state.[16]

Delayed Fluorescence. When the exciting light is sufficiently intense, delayed fluorescence is observed at exactly the same location as the fluorescence. Since we previously analyzed the decay of the delayed fluorescence and confirmed that it originated from the triplet–triplet annihilation,[4] we did not repeat this experiment in the present paper. In the level of the low exciting light that we worked with in the present paper, the delayed fluorescence was almost invisible.

Temperature Dependence of the Phosphorescence Intensity. The sharp phosphorescence we have observed at 4.2 K is completely quenched at 77 K. In order to understand the mechanism of the thermal quenching, we measured the temperature dependence of the intensity. The temperature dependence of the phosphorescence intensity of (SiMePr)$_n$ at its peak (361 nm) is shown in Figure 4. Open circles are the experimental data, and the solid curve is the theoretical fit in terms of a model discussed below. The phosphorescence intensity remains constant in the temperature range of 4.2 to ~10 K; however, above 10 K the intensity begins to decrease and the phosphorescence is almost completely quenched at ~30 K. Similar temperature dependence was observed for the other polysilylenes.

The observed temperature dependence is analyzed in terms of a model that is schematically shown in Figure 4. In this model, a quenching level exists at energy ΔE above the emitting level. The kinetics for the population of the emitting level N_1 and that of the quenching level N_2 are expressed as follows.

$$\frac{dN_1}{dt} = -N_1\left(K\exp\left(-\frac{\Delta E}{kT}\right) + k_1\right) + N_2K + F_1 \quad (1)$$

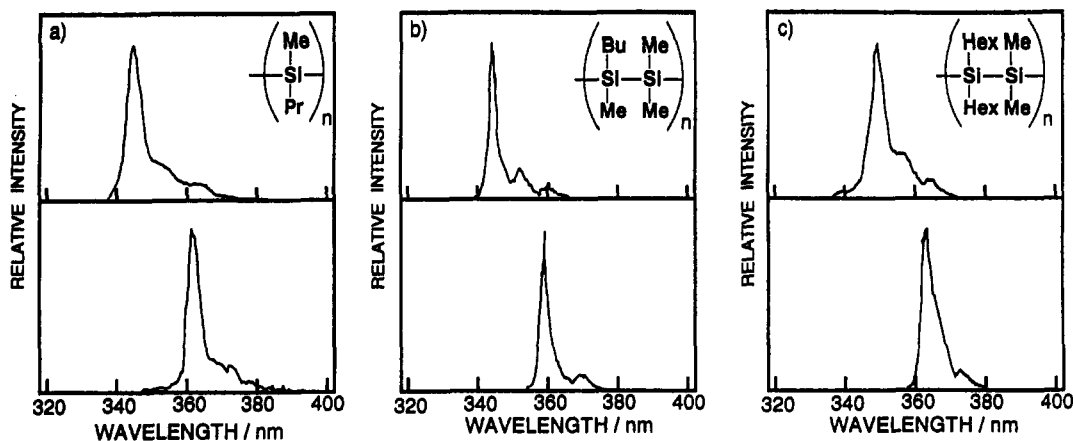$$\frac{dN_2}{dt} = N_1K\exp\left(-\frac{\Delta E}{kT}\right) - N_2(K + k_2) + F_2 \quad (2)$$

Figure 3. Fluorescence and phosphorescence of benzene solutions of $(SiMePr)_n$, $(SiMeBuSiMe_2)_n$, and $(SiMe_2SiHex_2)_n$ observed at 4.2 K.
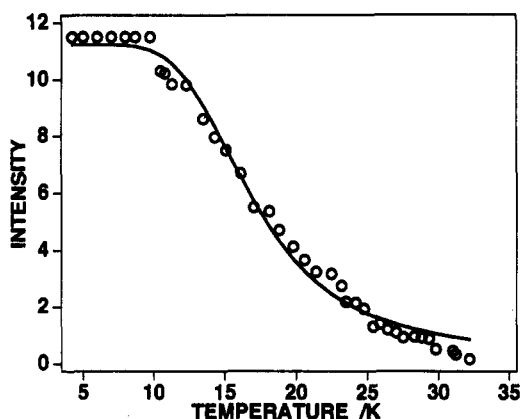

Figure 4. Temperature dependence of the phosphorescence intensity of $(SiMePr)_n$. Open circles are the experimental points, and the solid curve is the best fit based on the thermal quenching model described in the text.

TABLE I: Fluorescence Peaks, Phosphorescence Peaks, and the Energy Differences between the Peaks (ΔE_{ST}) for $(SiMePr)_n$, $(SiMeBuSiMe_2)_n$, and $(SiHex_2SiMe_2)_n$

polymer	fluorescence peak/nm	phosphorescence peak/nm	ΔE_{ST}/ cm^{-1}
$(SiMePr)_n$	344	361	1.4×10^3
$(SiMeBuSiMe_2)_n$	343	359	1.3×10^3
$(SiMe_2SiHex_2)_n$	348	364	1.3×10^3

F_1 and F_2 account for the direct excitation. By making the steady-state approximation for N_1 and N_2, we obtain the following expression for the intensity of the phosphorescence[17]

$$I = \frac{1}{c_1 \exp\left(-\dfrac{\Delta E}{kT}\right) + c_2} \qquad (3)$$

where

$$\frac{c_1}{c_2} = \frac{Kk_2}{(K + k_2)k_1} \qquad (4)$$

The observed temperature dependence was analyzed in terms of the above scheme, and the solid curve in Figure 5 is the result of the best fit. The energy gap ΔE thus determined is 63.3 cm^{-1}.

The temperature dependence of the phosphorescence intensity was also analyzed recently by Walsh et al.[6] for poly(dihexylsilylene). These authors plotted the logarithms of the intensity against the reciprocal temperature, and the plots are linear only at higher temperature regions and level off at lower temperature regions. This behavior is analogous to the temperature dependence described above, and is probably better explained by the above model.

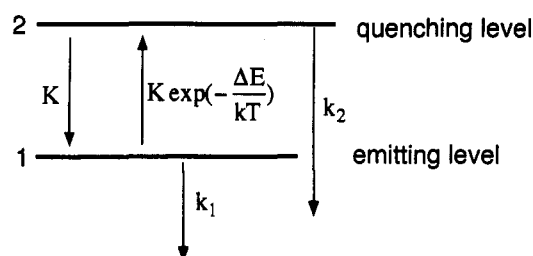The nature of the quenching level is not known at present. However, from the analogy of similar temperature dependences,[17]

Figure 5. Model for the thermal quenching.

we surmise that the quenching level is associated with the completely delocalized band state of the polymer. This subject will be further studied in later publications.

References and Notes

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