INTRAMOLECULAR EXCIPLEX FORMATION IN AMMONIUM-TYPE AMPHIPHILIC POLYSILANES

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Abstract

Fairly broad emission in the visible region was observed for poly(methylphenylsilane) bearing an ammonium substituent both in solutions and in thin films. The appearance of this low-energy emission (not due to a $\sigma* \rightarrow \sigma$ transition) is reasonably explained by considering the intramolecular exciplex formation between a Si-conjugated main chain and an ammonium site in the same monomer unit. The relaxation dynamics involving the emission should be determined by the different distance.

1 Introduction

High molecular-weight polysilanes have been extensively studied because of their unique photo- and radiation-sensitive properties attributed to the delocalized s-electron in the Si backbone [1]. To date, these studies have been limited in the bulk materials or in organic solutions, since intricate procedures are required for introduction of hydrophilic moieties into the polysilane substituents. Recently, chemically modified amphiphilic polysilanes with an ammonium moiety were synthesized and utilized for constructing Langmuir-Blodgett films by Seki et al. [2]. In addition to their spectroscopic studies, we have just reported the first observation of the emission from the excited complexes formed in this family of amphiphilic polysilanes [3]. This paper describes our expanded investigation, presenting the results of a detailed study of the molecular interaction in the ammonium-type polysilanes.

2 Experimental

For purposes of comparison, five kinds of amphiphilic polysilanes indicated in Chart 1 (**PS1**-**PS5**) were synthesized according to the established procedure [2] and examined for spectroscopy. Spectral measurements at room temperature were made on chloroform solutions at the concentration of about 1×10^{-4} Si-unit mol dm^{-3}. A energy-minimization calculation of the ground-state conformation was carried out to predict stable main- and side-chain orientations in polysilanes under study. The structure and the energy employed in the calculation were based on the molecular mechanics program MM3 (AccuModel v1.1 from MicroSimulations) [4]. We used a model compound consisting of a single chain of five Si atoms.

3 Results and Discussion

Fig.1 presents the emission spectra observed for methylphenylsilane-based (**PS3**, a), methylbenzylsilane-based (**PS4**, b), and methyl[β-phenethyl]silane-based (**PS5**, c) polymers in the chloroform solution. Each polysilane examined here has a C_{14} alkyl chain in the side ammonium group. These spectra displayed an intense and sharp emission band centered at 325-355 nm (with small Stokes shifts, about 0.3 eV), which is due to a $\sigma* \rightarrow \sigma$ transition of the Si backbone [1]. Strikingly, another broad emission band around 400-500 nm was observed only for **PS3**. It is well-known that linear polysilane derivatives never show a visible emission like this except for a weak, broad phosphorescence or an impurity band only in rigid media (at ≈ 77 K) [5]. Thus, we have considered the possibility of intramolecular interaction as an origin of the new band, since intermolecular interaction may be negligible in the case of the diluted solution systems in which molecules are supposed to be isolated from each other. In the previous study [3], we assumed that excited complexes which an ammonium moiety form with a σ-conjugated segment in the same unit would lead to the appearance of the broad emission in the visible region.

The minimum-energy conformation obtained for **PS3** is illustrated in Fig.2. In the conformation, the center-to-center distance between the ammonium group and the Si in the same monomer unit was 6.3 Å, whereas those for **PS4** and **PS5** were 7.7 and 9.7 Å, respectively. In line with the above discussion, we have considered that the different Si-ammonium distance essentially determines the photophysical behavior of the three polysilanes. Thus, the difference in the spectral profiles of Fig.1 is simply explained as follows. The exciplex cannot be formed in **PS4** and **PS5**, in which the methylene chain is directly bonded to the polymer backbone keeps the ammonium site from overlapping the Si orbital in the same monomer unit. In contrast, the exciplex can be formed in **PS3** because the complex-forming parts easily approach each other, and an efficient overlap between their orbitals is acquired.

References

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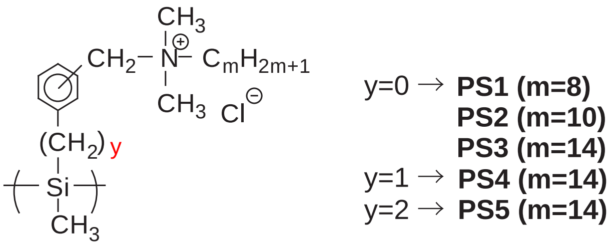

Chart 1. Structures and abbreviations of the polysilanes used in this study.

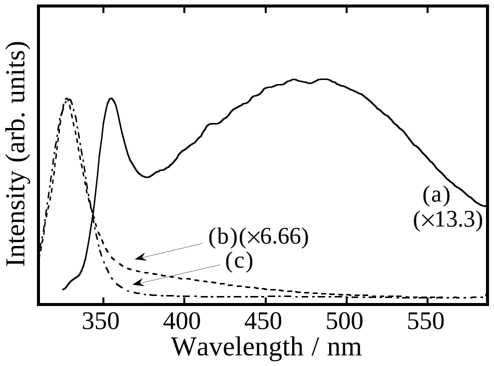

Fig.1. Emisson spectra of methylphenylsilane-based **PS0** (a), methylbenzylsilane-based **PS1** (b) and methyl[β-phenethyl] silane-based **PS2** (c) polymers in chloroform solutions (ca. 1×10^{-4} Si-unit mol dm^{-3}).

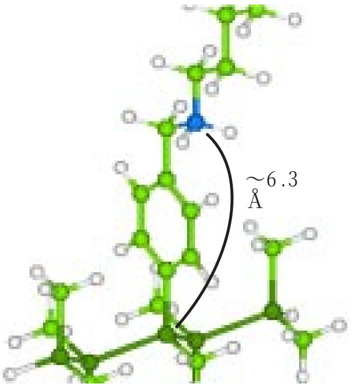

Fig.2. The most probable conformation of **PS3**, along with the distance between the nearest Si-ammonium pair in the ground state. The energy minimization was performed on both the main- and side-chain orientations.