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Exciplex emission from amphiphilic polysilanes bearing ammonium moieties

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Abstract

We were the first to observe two emission bands in the visible region for some kinds of ammonium-type amphiphilic polysilanes both in solutions and in thin films. One, a broad emission band at 400–500 nm not due to a $\sigma^* \to \sigma$ transition, was observed only for methylphenylsilane-based polymer solutions. The appearance of this low-energy emission is reasonably explained by considering the *intra*molecular exciplex formation between a Si-conjugated main chain and an ammonium site in the same monomer unit. The other, an emission band at the longer wavelength (around 560 nm), was found in the solvent-cast films where each molecule is randomly located, in addition to that observed for the solutions. This emission, which was not observed for the oriented LB films, is considered to originate from an *inter*molecular interaction. © 1997 Elsevier Science B.V.

1. Introduction

Polysilanes [$-(\mathrm{SiR_1R_2})_n-$], whose backbone consists only of silicon atoms, have received increasing attention, because of their characteristic optical and electronic properties [1]. For example, this new class of polymers exhibits large non-linear optical effects, photodegradation, photoconduction, etc. These properties have been attributed to the extensive delocalization of the σ electrons, which is strongly influenced by the backbone conformations [1,2]. To date, although much effort has been devoted to the evaluation of the polysilane properties, these studies have been limited to bulk materials or solutions. It is because the organic substituents on the Si were restricted to hydrophobic groups such as alkyl and aromatic in the polymerization reaction. Chemically modified amphiphilic [3–7] or alkoxyl-group containing [8,9] polysilanes have been recently synthesized and utilized for constructing Langmuir–Blodgett (LB) films by some research groups. Among the LB-forming polymers, we have focused on polysilanes bearing a long-chain ammonium substituent which were first prepared by Seki et al. [3]. Their work also revealed the spectroscopic properties of these polysilanes both in solutions and in LB films to some extent [4–6]. Nevertheless, the characteristics of the excited states in the polysilanes have not been clarified so far. The relaxation process of these excited chromophores, whose study provides insight into the mechanisms of charge and energy transport therein, is largely determined by their environment originating from molecular interaction in the polymers. The knowledge on this subject is, therefore, of great importance in view of the applicability of polysilane thin films to optical devices.

We report herein the results of our spectroscopic study, involving the LB method using the six ammonium-type amphiphilic polysilanes indicated in Plate 1 (**PS1–PS6**). For the film samples, we also observed the emission induced by ion-beam bombardment under the condition

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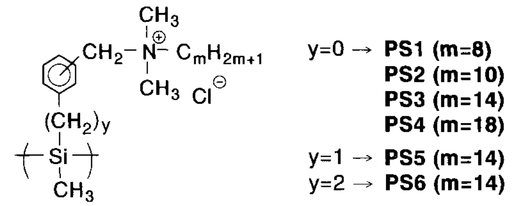

Plate 1. Structures and abbreviations of the polysilanes used in this study.

that the Si main chain should not be decomposed. This paper describes, for the first time, the observation of the emission from excited complexes formed in some of the amphiphilic polysilanes adopted in the present study.

2. Experimental section

2.1. Materials

The ammonium-containing amphiphilic polysilanes were prepared following the procedure adopted by Seki et al. [3]. The silane monomers of methylphenyldichlorosilane and methyl[β-phenethyl]dichlorosilane for **PS1–PS4** and **PS6** were purchased from Shin–Etsu Chemical Co. and distilled before use. For synthesis of **PS5**, methylbenzyldichlorosilane monomer was prepared by condensation of the corresponding benzyl Grignard reagent with methyltrichlorosilane. The starting polymers were synthesized from these three monomers by the conventional Wurtz coupling. The phenyl group was chloromethylated as described by Ban et al. [10] and then quaternized with a tertiary N,N-dimethylalkylamine in tetrahydrofuran at refluxing temperature (65°C) for 15–20 h. In particular, the quaternization reaction of the methylphenylsilane-based polymers was performed using N,N-dimethylalkylamine whose long-chain alkyl group varied from octyl- ($m = 8$) to octadecyl- ($m = 18$) to provide the polysilanes of **PS1–PS4**. The ^{1}H-NMR and GPC measurements were done during the intermediate and final steps.

2.2. Methods

LB-film fabrication was performed with a Lauda FW-1-M film balance under dimmed red light to avoid decomposition of the polymers. The chloroform solution of the obtained polysilane ($\sim 1 \times 10^{-3}$ Si-unit mol dm^{-3}) was spread on water which was doubly distilled and then passed through a Milli-Q system. The monolayer on the subphase water compressed to 30 mN m^{-1} was transferred onto a Si substrate by the vertical dipping technique. The transfer ratios for all deposition processes were high enough to prepare the specimens, which is identical to the previous results [3–5].

UV–vis absorption and emission spectra were recorded using a Hitachi U-3200 and a Hitachi F-3000 spectrometers, respectively. Excitation at 300 nm was carried out by a 150 W Xe lamp. All these measurements were made on the chloroform solutions prepared at a concentration of about 1×10^{-4} Si-unit mol dm^{-3} in room temperature. The ion beam used in ion-induced emission measurement of the film samples, i.e., a solvent-cast film and a prepared LB film, was 2 MeV H$^+$ beam generated from a Van de Graaff accelerator at the Research Center for Nuclear Science and Technology, The University of Tokyo. The details of the measurement system were previously published [11].

3. Results and discussion

3.1. Spectroscopy of prepared organic solutions

3.1.1. UV absorption

Fig. 1 displays the UV–vis absorption spectra of all the polysilanes (**PS1–PS6**) in the chloroform solutions. An intense band originating from the conjugated Si–Si backbone [1,2] appears at 300–330 nm (except for **PS4**). The position of the absorption onset was shifted to longer wavelengths for the methylphenylsilane-based polymers (**PS1–PS4**) compared to those for the polysilanes from the other monomers (**PS5** and **PS6**). It is well-known that these bathochromic shifts are observed for polyorganosilanes with bulky substituents such as the aromatic group, mainly because the ratio of the *trans–trans* conformer in the Si backbone increases [1,5].

Notable results hereof are in the spectral shape of **PS4**, which is in contrast to that of polymers having shorter-length alkyl chains in the ammonium moiety. **PS4** shows a broad absorption with no peak at a slightly shorter wavelength than **PS1–PS3**. Zeigler et al. [12], in the study on similar UV absorption features of alkyl- and aryl-substituted polysilanes, reported that the spectral change was

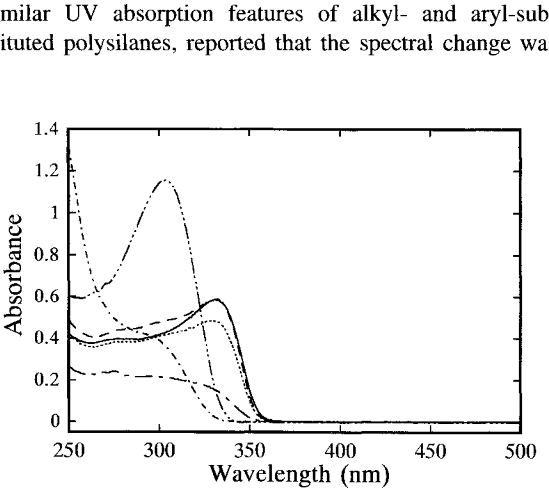

Fig. 1. UV–vis absorption spectra of **PS1** (————), **PS2** (---), **PS3** (— — — —), **PS4** (— — —), **PS5** (- · -) and **PS6** (-----) in chloroform solution ($\sim 1 \times 10^{-4}$ Si-unit mol dm^{-3}).

due to the conformational inhomogeneity. They additionally suggested that the substituent-size dependence was due to steric interference between pendant groups, which could result in Si–Si bond lengthening and/or change in the equilibrium content of the *trans* and *gauche* conformers. Accordingly, we considered that, in the present case, the longest C_{18} chain in **PS4** may fix the backbone conformation to an unstable state (namely, enhancement of the *gauche* conformer in the Si backbone). Its steric hindrance can lead to the partial destruction of the extensive electronic conjugations along the Si chain.

3.1.2. Emission

Fig. 2 presents the emission spectra observed for methylphenylsilane-based (**PS3**, a), methylbenzylsilane-based (**PS5**, b), and methyl[β-phenethyl]silane-based (**PS6**, c) polymers in the chloroform solutions. 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]. The longer-wavelength shift of the emission observed for **PS3** is in good accordance with the bathochromic shift of the UV absorption.

Strikingly, another broad emission band around 400–500 nm was observed only for **PS3**. This broad band is in contrast to the sharp fluorescence arising from the backbone delocalized state as cited in the above paragraph. Generally, 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) [12,13]. In the following section, we will discuss the assignment of this new band.

The emission spectra of methylphenylsilane-based polymers bearing different length of alkyl chains in the ammonium group (**PS1–PS4**) are shown in Fig. 3. Only **PS4**, whose backbone conformation is the unstable state to cause the above mentioned absorption property, had no main-chain emission in the near-UV region. Except for this polysilane, the emission band in the visible region seems to be red-shifted with an increase in the carbon-chain length from C_8 (**PS1**) to C_{14} (**PS3**). The apparent spectral shift resembles the photophysical behavior of the exciplexes formed between aromatic hydrocarbons and aliphatic amines in that the emission energy closely depends on the alkyl-chain length in the amines [14,15]. Further, these series of polymers showed no absorption other than that originating from the σ-conjugated main chain, as can be seen in Fig. 1, which indicates that no specific interaction exists in the ground state. This observation is also characteristic of general exciplex formation [14,15]. In the case of the diluted solution systems in which molecules are supposed to be isolated from each other, *inter*molecular interaction may be negligible. Thus, we considered the possibility of *intra*molecular interaction in which an ammonium moiety is involved, as an origin of this emission band.

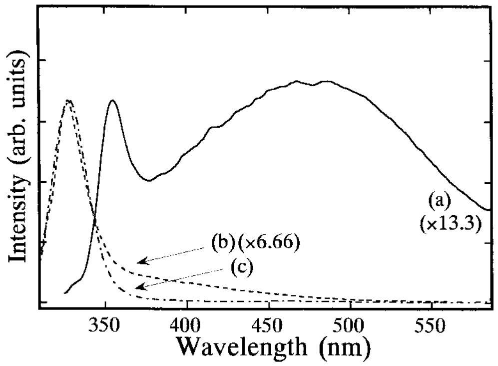

Fig. 2. Emission spectra of methylphenylsilane-based **PS3** (a), methylbenzylsilane-based **PS5** (b) and methyl[β-phenethyl]silane-based **PS6** (c) polymers in chloroform solution (~ 1×10^{-4} Si-unit mol dm^{-3}). The excitation wavelength was 300 nm.

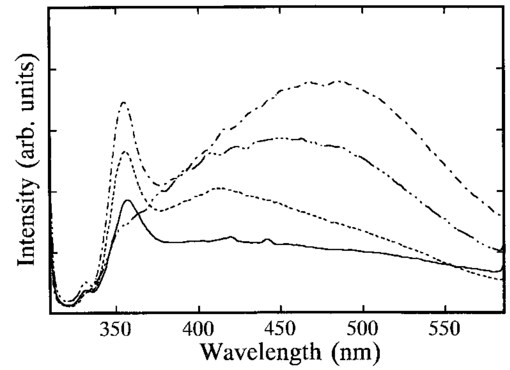

Fig. 3. Emission spectra of the series of methylphenylsilane-based amphiphilic polymers having different length of alkyl chains in the side ammonium group. This figure contains curves of **PS1** (————), **PS2** (- - -), **PS3** (– · –), and **PS4** (– – – –) in chloroform solution.

Obviously in Figs. 2 and 3, only methylphenylsilane-based polymers **PS1–PS4** showed the broad band. This finding suggests that a difference in side-group structure (i.e., methylene-chain length between the Si and an aromatic group in the same monomer unit) determines the generation of the *intra*molecular interaction possibly responsible for the visible emission. Therefore, we assumed the model that excited complexes which the ammonium moiety form with the σ-conjugated segment (*not* with the aromatic site) would lead to the appearance of the broad emission in the visible region. According to this model, what is called, the '*exciplex model*', the difference in the spectral profiles of Fig. 2 is simply explained as follows. The exciplex cannot be formed in **PS5** and **PS6**, in which the methylene chain is directly bonded to the polymer backbone keeps the ammonium site from overlapping the

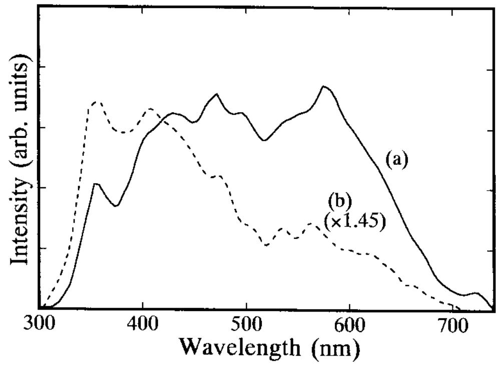

Fig. 4. Ion-induced emission spectra of a solvent-cast film (a) and a 701-layered LB film (b) of the amphiphilic polysilane **PS3** on a Si substrate. The fluences of 2 MeV H^+ were 0.12 μC/cm^2 for (a) and 0.16 μC/cm^2 for (b), respectively.

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.

The explanation presented here is also supported by the following experimental results. (i) As shown in Fig. 3, the visible emission of **PS4** was blue-shifted compared to **PS3** which has a C_{14} alkyl chain. This is inconsistent with the alkyl-chain length dependence of the emission energy observed for **PS1–PS3**. The different behavior seems to correspond to the unusual shape of its absorption spectrum mentioned above. If so, the emission under discussion is closely related to the electronic structure of the Si skeleton. (ii) Our preliminary experiments revealed that this visible emission declined together with a decrease in the $\sigma^* \rightarrow \sigma$ emission due to main-chain decomposition during photoexcitation. There should be a strong correlation between the two emitting states.

3.2. Ion-induced emission of transferred LB multilayers

The ion-induced spectra recorded from a solvent-cast film (a) and a 701-layered LB film (b) of the polysilane **PS3** on a Si substrate are depicted in Fig. 4. These spectra were measured at the initial irradiation stage, where the irradiation damage is negligible (the ion fluences were 0.12 μC/cm^2 for (a) and 0.16 μC/cm^2 for (b), respectively). Obviously in Fig. 4, another broad emission band at the longer wavelength (around 560 nm) was found only in the solvent-cast film, while both films showed 400–500 nm emission which was also observed for the solutions. It is possible that this spectral discrepancy would be ascribed to a difference in molecular ordering between the two films. Therefore, to present a plausible explanation for the appearance of this emission, we considered the interaction between adjacent molecules in the excited state. In line with the above discussion, the band is assumed to originate from the *inter*molecular exciplex formation prior to emission although the possibility that the emission process might involve some complexities cannot be entirely excluded. On the basis of this assumption, the LB film in which each molecule is expected to align parallel to the dipping direction did not exhibit the emission because the *inter*molecular distances were constantly so great that the complex could not be formed. On the other hand, in the solvent-cast film where each molecule is randomly located, an ammonium site in one molecule can be incidentally close to a Si conjugated segment in a neighboring molecule, so that the efficient overlap between their orbitals is established. Only under this condition, would it lead to *inter*molecular exciplex formation.

4. Conclusions

We synthesized various kinds of amphiphilic polysilanes bearing a trimethyl-ammonium substituent which are expected for constructing LB films, and then investigated their spectroscopic properties in detail. In the emission spectra of chloroform solutions, a broad emission around 400–500 nm other than that via the σ^* delocalized state was newly observed only for methylphenylsilane-based amphiphilic polysilanes. The appearance of this low-energy emission is explained by considering the *intra*molecular exciplex formation between an ammonium moiety and the Si-conjugated main chain. Based on this model, it follows that the exciplex cannot be formed in the case where the methylene chain is directly bonded to the polymer backbone because of the inefficient overlap of the ammonium site with the Si orbital in the same monomer unit. Another emission around 560 nm was observed for the random casted films in addition to that observed for the solutions. This emission, which was not observed for the oriented LB films, would originate from *inter*molecular interaction, that is, the excited complex formed between an ammonium site in one molecule and a Si conjugated segment in a neighboring molecule.

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