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Spectroscopic Observations of Surfactant-Induced Conformational Changes of a Water-Soluble Polysilane

Takahiro Seki,* Atsushi Tohnai,[†]
Takashi Tamaki,[‡] and Akira Kaito[‡]

Research Laboratory of Resources Utilization,
Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku,
Yokohama 226, Japan, Fine Chemicals Research Center,
Catalysts & Chemical Industries Co. Ltd., 1-13
Kitaminato-cho, Wakamatsu-ku, Kitakyushu 808, Japan,
and National Institute of Materials and Chemical Research,
1-1 Higashi, Tsukuba, Ibaraki 305, Japan

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Interaction of surfactants with water-soluble polymers has long been a matter of great interest due to its highly cooperative binding nature and importance in mimicking protein/biomembrane systems.[1] Utilization of spectroscopic probes such as solvatochromic dyes[1−3] and fluorescence probes[1,4,5] provides useful information on microenvironmental changes caused by the surfactant binding. Such surfactant binding is known to induce conformational changes of the polymer backbone.[1] However, spectroscopic observations using extrinsic probes, in general, do not give direct knowledge on the backbone conformation. For synthetic polypeptides and proteins, on the other hand, straightforward knowledge on the conformational state is available by circular dichroism and optical rotational dispersion. These optical measurements have revealed surfactant-induced transitions of the secondary structures of polypeptides.[6−9]

We have recently developed a cationic water-soluble polysilane (polysilylene) bearing a trimethylammonium group in the side substituent (APS, poly[methyl-{2-(((trimethylammonio)methyl)phenyl)ethyl}silane chloride], Chart 1).[10,11] Among the vast variety of polysilanes hitherto synthesized, APS is, to our knowledge, the first example of a fully water-soluble charged polysilane.[12] Polysilane materials show strong light absorption in the UV region and efficient fluorescence, which are attributed to the delocalized σ electron along the Si backbone.[13] The above optical properties are highly sensitive to the population of *trans* and *gauche* conformers involved. Due to the flexible nature of the single-bonded Si chain, the conformation state should be susceptible to environmental perturbations. Extension of the conformation in which the *trans* conformer segment is enriched is known to cause bathochromic shifts in the UV absorption.[10,14,15] For unsymmetrically substituted polysilanes such as APS, continuous spectral shifts are observed.[8−13] In this communication, we report on the optical observations of the conformational changes of APS that are induced by binding of sodium dodecyl sulfate (SDS) in water. It is found here that a stoichiometric correlation is attained between the binding amount of SDS and the optical changes of APS.

The synthesis of APS (M_w = ca. 2.6×10^4) was described elsewhere.[10,11] APS was dissolved in distilled water (1.0×10^{-4} unit mol dm^{-3}), and a 2.5-mL portion was placed in a 1-cm square quartz cell. Aliquots of a SDS (Wako Pure Chemicals Co.) stock solution dissolved in distilled water (3.6×10^{-2} mol dm^{-3}) were added to this APS solution with a microsyringe and agitated for 1 min using a magnetic stirrer. The concentration of SDS was changed by sucessive additions of the SDS stock solution. The UV−visible absorption and fluorescence measurements were carried out using a Shimadzu UV-160 and a JASCO FP-777 spectrometer, respectively, at 20 ± 1 °C.

Chart 1

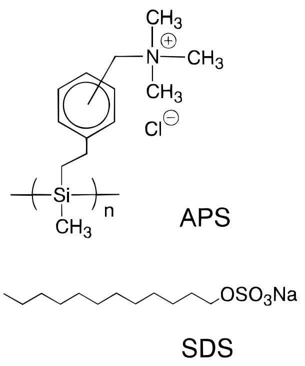

Figure 1 shows UV−visible absorption spectra of APS in pure water and in the presence of SDS at various concentrations. The broad absorption band observed near 300 nm corresponds to the $\sigma-\sigma^*$ transition of the Si backbone. The broadened spectra should indicate the existence of an inhomogeneous segmental geometry in the APS backbone in aqueous solutions. The addition of SDS led to bathochromic shifts of this band and changes in the absorbance at the peak wavelength. The absorption band in pure water gave a maximum at 286 nm. This peak position is in close agreement with those reported for nonionic water-soluble polysilanes bearing a tri- or tetra(ethylene oxide) moiety (287−288 nm)[12a] instead of the ammonium-containing phenyl group in the APS molecule.

Figure 2 indicates the profiles of the peak position of the $\sigma-\sigma^*$ absorption band (a) and the absorbance at these wavelengths (b) as a function of SDS concentration. The absorption peak was abruptly shifted to longer wavelengths by addition of SDS in lower concentration regions (Figure 2a). An inflection was observed in this profile near a concentration of 1×10^{-4} mol dm^{-3}, which corresponds to the equimolar amount of the ammonium group of the APS unit (indicated by an arrow in the figure). Beyond this concentration, the absorption peaks were positioned at constant wavelengths near 300 nm. This behavior implies that the conformation of APS in pure water is extended by addition of SDS up to the stoichiometric amount.

The absorbance exhibited a sharp rise and reached a maximum when the stoichiometric amount of SDS was added (Figure 2b). The decrease in the absorbance in higher SDS concentration regions beyond the equimolar condition is probably due to evolution of slight turbidity. A development of precipitates which are clearly recognized by the naked eye occurred occasionally beyond the stoichiometric concentration. In such cases, decreases in the absorbance became more manifest. Precipitate formation near stoichiometric concentrations is in agreement with those reported in previous observations by Goddard and Hannan[16] for SDS binding with cellulose-based ammonium-containing polymers. In the present system, the precipitate evolution was not reproducible.

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* To whom correspondence should be addressed at the Tokyo Institute of Technology; phone/fax: +81-45-924-5247, e-mail: tseki@res.titech.ac.jp.

[†] Catalysts & Chemical Industries Co. Ltd.

[‡] National Institute of Materials and Chemical Research.

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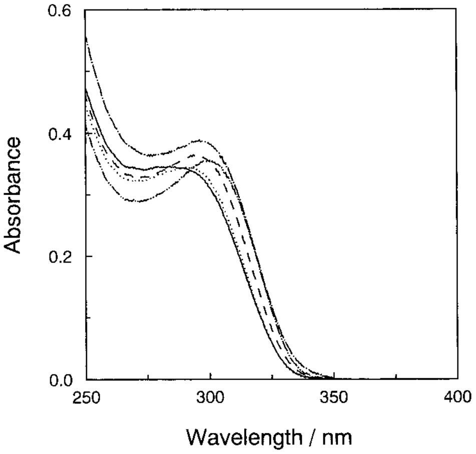

Figure 1. UV–visible absorption spectra of APS in distilled water at various SDS concentrations. The concentration of APS was 1.0×10^{-4} unit mol dm^{-3}. The concentrations of SDS were 0 (—), 1.4×10^{-5} (···), 4.3×10^{-5} (— — —), 1.2×10^{-4} (—·—), and 7.1×10^{-3} (—··—) mol dm^{-3}.

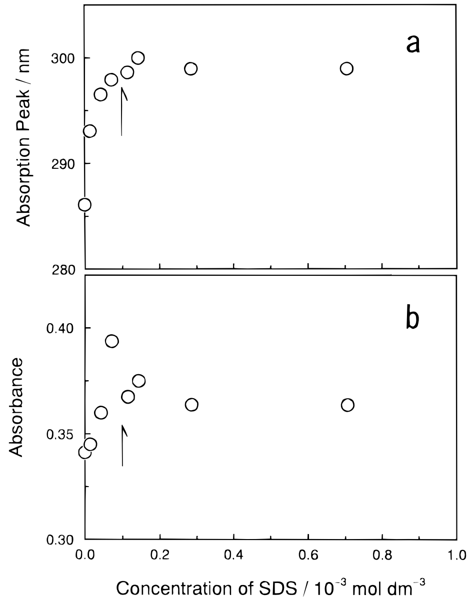

Figure 2. Profiles of the peak position of the σ–σ^* absorption band (a) and the absorbance at these wavelengths (b) as a function of SDS concentration. The arrow indicates the concentration of the ammonium unit of APS (1×10^{-4} mol dm^{-3}).

Fluorescence properties were much more sensitive to the SDS binding process. Figure 3 depicts fluorescence spectra of APS with excitation at 280 nm at various SDS concentrations.[17] An abrupt enhancement in the fluorescence intensity was observed upon addition of SDS up to the equimolar amount. The fluorescence near the stoichiometric addition of SDS was enhanced by a factors of ca. 4 from that in pure water. The shift of the emission peak due to SDS binding was not significant, but shifts to longer wavelengths of a few nanometers were observed (336 → 339 nm). The excitation spectra monitored at 335 nm in the absence and presence of SDS gave a peak at 316–318 nm. The bathochromic shifts from those of the absorption spectra (ca. 300 nm) suggest that the singlet state excitation energy is emitted from the segments of the lowest energy, probably in the all-*trans* conformation.[18]

Changes in the UV absorption and fluorescence spectra observed here closely resemble those in the water–ethanol binary mixtures.[11] In the binary solvent systems, addition of ethanol to an aqueous solution of APS leads to both bathochromic shifts of the σ–σ^* absorption band and large increases in the fluorescence intensity. We assume that SDS-bound APS experiences similar environments to those in water–ethanol mixtures.

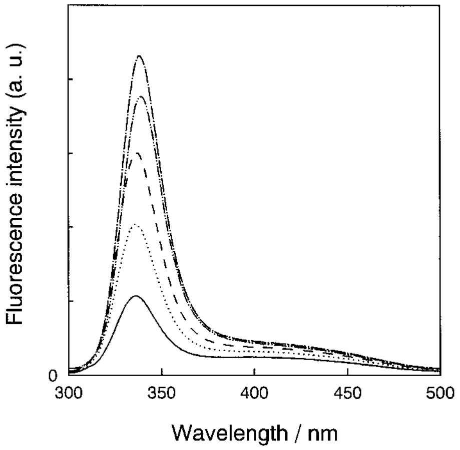

Figure 3. Fluorescence spectra (uncorrected) of APS in distilled water at varius SDS concentrations with excitation at 280 nm. The concentration of APS was the same as indicated in Figure 1. The concentrations of SDS were 0 (—), 1.1×10^{-5} (···), 2.7×10^{-5} (— — —), 7.6×10^{-5} (—·—), and 10×10^{-5} (—··—) mol dm^{-3}.

It is supposed here that addition of SDS induces extension of the APS conformation. This behavior may be rather conflicting in consideration of the charge neutralization which should give a more hydrophobic complex. This process is likely to induce a more compact conformation of APS in water. However, a theoretical consideration predicts that surfactant binding to a flexible polymer induces rigidity at high binding ratios, and this change leads to conformational changes from a coil-like to a rod-like state.[19] This stiffening is attained sterically by association and crowding of the surfactant molecules that are absorbed onto the polymer. Our spectroscopic observations are in line with this theoretical evaluation.

In summary, surfactant-induced conformational changes of the water-soluble polysilane in the aqueous system were directly observed by UV absorption and fluorescence spectroscopy. These findings imply that polysilane materials may find significance in the application to molecular assembly systems in aqueous solutions in addition to the widespread organic-solvent and solid film systems.

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