Solvatochromic Properties of an Ammonium Containing Polysilane in Water-Ethanol Binary Mixtures

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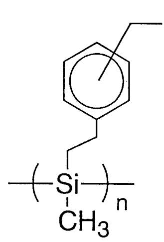
A water-soluble polysilane having a trimethylammonium group has been synthesized and its spectroscopic properties in water, ethanol and their binary mixtures are investigated. In water-ethanol binary mixtures, variations in the UV absorption and fluorescence properties attributed to the delocalized σ electron in the Si backbone exhibit a maximum at intermediate mixing ratios.

Polysilanes are attracting increasing attention as a new class of polymers which possess unique conformation-dependent photosensitive properties attributed to the delocalized σ orbital electron.[1,2] Although a vast amount of data on chromic properties has been accumulated,[1,2] these studies are limited in organic solutions[3] or solid film systems. This is due to requirement of intricate procedures for introduction of hydrophilic moieties in the substituents on polysilanes. Chemically functionalized polysilanes such as amphiphilic[4-6] or ether-bond containing[7,8] materials have recently been synthesized and utilized for assembling Langmuir-Blodgett multilayers.[9] These works are positioned at the starting point of water-relevant research in polysilane chemistry. Nevertheless, optical properties of fully water-soluble polysilanes have not been reported so far.[10] This letter describes, for the first time, the spectroscopic features of a ionic water-soluble polysilane. The polysilane used in this work bears a trimethylammonium moiety in the side substituent (APS).[11,12] We wish to show our preliminary results on characteristic properties of UV absorption and fluorescence of APS in pure and mixed water-ethanol binary solvent systems.



APS

The concentration of APS was 1.0×10^{-4} unit mol dm^{-3} in all solvents. For binary mixtures, two stock solutions of APS dissolved in pure water and ethanol at the identical concentration was mixed at various ratios. UV-visible absorption and fluorescence spectra were recorded on a Shimadzu UV-160 and a JASCO FP-777 spectrometers, respectively. Both measurements were carried out with a 1-cm quartz cell at 20 ±1 °C.

Figure 1 shows the UV-visible absorption spectra of APS in water-ethanol binary mixtures at various volume mixing ratios (x). The spectral shape was modulated as the solvent composition was changed. The inset of the figure indicates the peak position of the σ - σ * band as the function of x. The inset clearly shows that the peak position of this band ranging 280 - 304 nm was shifted to longer wavelengths in mixed solvents than those in pure water or ethanol. It is known that the this absorption band shows bathochromic shifts when the ratio of the *trans/gauche* conformer in the Si backbone increases, namely, the conformation of the Si backbone is in more extended states.[5,13]

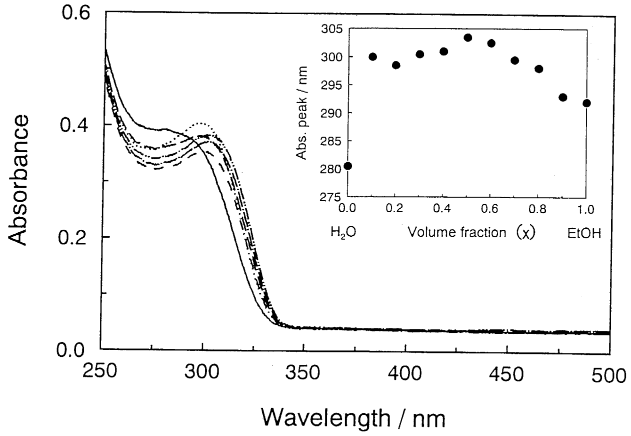


Figure 1. UV-visible absorption spectra of APS in various water-ethanol mixtures. The mixing volume fractions (x) are 0.0 (———), 0.2 (— —), 0.4 (—··—·), 0.6 (—·—·), 0.8 (- - - -) and 1.0 (·········). The inset indicates the profile of the absorption peak position with the volume fraction (x).

Solvatochromic nature of APS became more manifest in emission properties. Figure 2 displays fluorescence spectra of APS taken with 280-nm excitation in the same solvent systems. The inset depicts the profiles of the emission peak wavelength (open circles)[14] and fluorescence intensity (closed circles) as the function of x. Both properties again gave variations exhibiting a maximum at the intermediate ratios with increase of x. The emission peaks were positioned at 331 - 338 nm. The longer-wavelength shift of emission observed here is coupled with the bathochromic shift of the UV absorption, and is in consistence with those observed for the discontinuous disorder-order conformational transition of poly(di-*n*-hexylsilane) (PDHS) in solid films.[15] Notable results were obtained in the fluorescence intensity. The fluorescence was enhanced by a factor of 13 at x = 0.6 from that at x = 0. This large enhancement does not seem to be explained simply by consideration of the conformational changes alone. According to data of Isaka and Matsumoto,[15] enhancement of the fluorescence intensity due to the conformational transition of PDHS can be estimated to be less than several factors. In the present systems, moreover, the solvent-induced continuous conformational changes should be much smaller than the PDHS film judging from small degrees of spectral shifts in the UV absorption (Figure 1). The emission peak showed the largest shift at x = 0.4, whereas the fluorescence intensity was highest at x = 0.6. This discrepancy also supports the involvement of some complexities in the emission process. The emission behavior observed here is not fully understood.

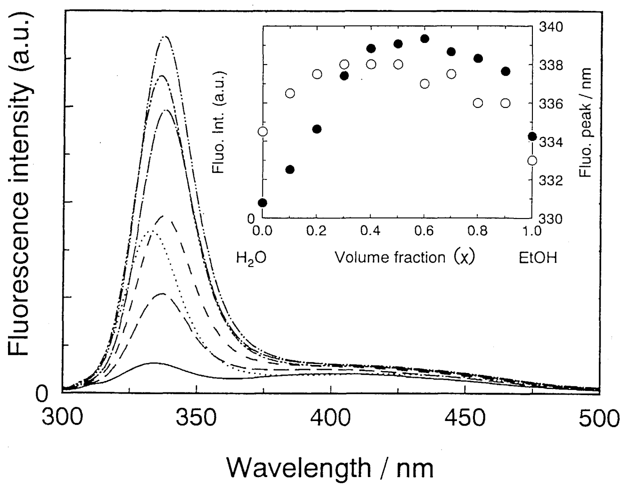


Figure 2. Fluorescence spectra of APS in various water-ethanol mixtures (excitation at 280 nm). The mixing volume fractions (x) are 0.0 (——), 0.1 (— —), 0.2 (– – –), 0.3 (–·–·), 0.6 (–··–··), 0.8 (-------), and 1.0 (·········). The inset shows the profiles of the fluorescence intensity (closed circles) and the fluorescence peak (open circles) with the volume fraction (x).

In any events, both results obtained by the UV absorption and emission measurements are in consistent with the picture that APS takes the most extended states at intermediate mixing ratios, x ranging 0.4 - 0.7 (corresponding to the mole fraction of 0.17 - 0.42).

The solvatochromic properties demonstrated here may be correlated with rheological observations which directly measure the states of polymer chain extension. As a pertinent example, the intrinsic viscosity of poly(methacrylic acid) in water-ethanol binary mixtures show maxima at the ethanol mole fractions ranging 0.3 - 0.7.[16] Such behavior can be interpreted as the consequences of solvation processes. In addition to this, structuring of the solvent itself, i. e., cluster formation of ethanol molecules in the water-ethanol binary mixtures, may influence the polysilane chain to find its most preferred conformation. Formation of polymeric clusters of ethanol molecules is known to be promoted to the largest extent at the ethanol mole fraction of ca. 0.4.[17]

In conclusion, spectroscopic properties, in particular emission behavior, of APS is found to be highly sensitive to the solvent composition of water-ethanol binary mixtures. Further investigation extending to other aqueous organic solvent systems is required for a better understanding of the present phenomena. Work in this regard is now in progress.

References and Notes

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11 In the previous investigation, this ammonium containing polysilane (APS) was used as the polyelectrolyte component of polyion-complex type Langmuir-Blodgett films: T. Seki, A. Tohnai, T. Tamaki, and K. Ueno, *J. Chem. Soc., Chem. Commun.*, **1989**, 1976.

12 APS was synthesized in the same manners as descried previously.[5] Fully chloromethylated poly[methyl(β -phenethyl)silane]5 (0.4 g, Mw = 2.1 x 104, Mw/Mn = 1.23) was dissolved in benzene (10 ml)/tetrahydrofuran (5 ml) mixed solvent, and trimethylamine gas was bubbled for 30 min. After being stirred at room temperature for 20 h, the precipitated polymer was collected. This white powder was washed with benzene three times and dried in vacuum to obtain 0.52 g of APS (in agreement with the calculated yield).

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14 A weak and broad emission was observed at 400 - 450 nm as indicated in Figure 2. We suppose that a small amount of crosslinking may occur during chloromethylation of the precursor polysilane. The broad emission could be ascribed to this energy trapping site.

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