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Effect of micelle structure on the spectral properties of poly(dimethylsilylene)

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The absorption and fluorescence spectral features of an intractable poly(silylene), poly(dimethylsilylene) (1), in aqueous micelles—attributable to an elongated *transoid* backbone conformation encompassed by three micelles—are discussed.

Poly(silylene)s are an interesting class of compounds because of an extended σ electron conjugation and have potential in applications including microlithography, photoconduction, *etc*.[1,2] The title compound, poly(dimethylsilylene) (**1**), is used as the precursor in the fabrication of incombustible silicon carbide fibers.[3] The properties of soluble poly(silylene)s have fully been established using various spectroscopic techniques.[1,2] However polymer **1** is intractable: it neither melts nor is soluble in any solvent and no spectral data is available.[4]

Surfactant molecules are known to form micelles in water and solubilize varieties of compounds including polymers.[5] Interaction of surfactants/micelles with water-soluble polymers has long been a matter of great interest due to their biomimetic nature.[6] In most of these studies, as the spectral features of polymers are insensitive to micelle–polymer interactions, the polymer–micelle interactions especially micelle induced conformational changes in the polymer backbone are difficult to understand. Even though extrinsic fluorescence probes, in general, do not give direct information about the backbone conformation, they have been used extensively to understand the microenvironmental changes associated with micelle–polymer binding.[6,7] Since the spectral properties of poly(silylene)s are conformational dependent,[1,2] poly(silylene) itself can be used as a probe molecule to understand the micelle–poly(silylene) interactions. Recently, Seki *et al*. have reported the effect of sodium dodecylsulfate (SDS) monomer molecules [not micelles, *i.e.*, the concentration range used is much lower than the critical micellar concentration (CMC) of SDS] on the absorption and fluorescence spectral properties of a water-soluble poly(silylene).[8] The addition of SDS monomers resulted in a small red shift in both the absorption and fluorescence spectra and an increase in the fluorescence intensity, resulting from conformational changes induced by the surfactant molecules. It is worth noting here that, the effect of monomeric surfactant molecules on the poly(silylene) backbone conformation is considerably less than that of the highly organized micelles and one can expect drastic changes in the poly(silylene) physical properties in the presence of micelles. In this communication, we have chosen an intractable poly(silylene) to understand its conformational dependent spectral properties in a few micelle solutions: Aerosol OT reverse micelles in hexane and aqueous micelles of sodium decyl- (SDES), dodecyl- (SDS) and hexadecylsulfates (SHS).[9]

Compound **1** shows micelle structure dependent spectral properties. In reverse micelles of Aerosol OT in hexane, compound **1** exhibits the absorption and fluorescence bands at 289 and 327 nm, respectively, whereas in aqueous micelles, a drastic red shift in both absorption and fluorescence spectra is noticed (Fig. 1 and Table 1). The observed red shift cannot be explained on the basis of solvent polarity owing to the polarity insensitive spectral properties of several soluble poly(silylene)s.[1,2] It seems reasonable that the micelle structure plays a crucial role on the poly(silylene) backbone conformation and hence on the spectral properties. To explain the spectral data in Aerosol OT, presumably, **1** should have the random-coiled structure [similar to that of other soluble peralkylpoly(silylene)s at room temperature in solution[2,4]] that should be wrapped around the reverse micelle(s) and hence be soluble in hexane. On the other hand, in aqueous micelles, the micelle induced an elongated *transoid* backbone conformation.[10] The absorption band of **1** corresponds to the σ→σ* (HOMO-LUMO) transitions.[1,2] The absorption spectrum is relatively broad compared to the fluorescence band. Full width at half maximum (FWHM)

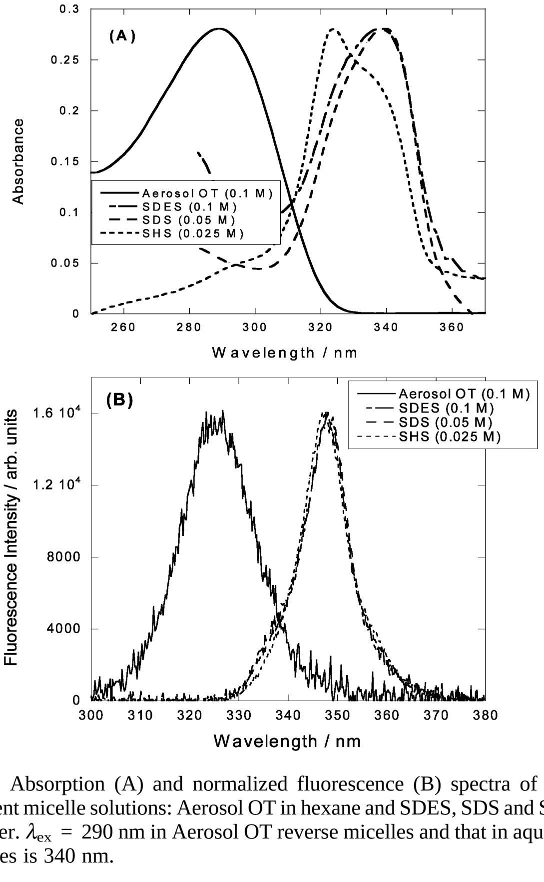

Fig. 1 Absorption (A) and normalized fluorescence (B) spectra of **1** in different micelle solutions: Aerosol OT in hexane and SDES, SDS and SHS, in water. λ_{ex} = 290 nm in Aerosol OT reverse micelles and that in aqueous micelles is 340 nm.

Table 1 Spectral properties of **1** in various micelles.

Micelle	λ_{abs}(max)/nm	λ_{flu}(max)/nm	$\Delta\nu^{b}$/cm^{-1}	ϕ_f
Aerosol OT	289	327	4,020	0.16[c]
SDES	324(sh)[a], 339	348	760	1.0
SDS	327(sh), 340	349	760	1.0
SHS	324, 340(sh)	347	2,045	0.78

[a] (sh) indicates shoulder, [b] Peak to peak, [c] see Ref. 9.

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for the absorption band of **1** in Aerosol OT is 7,050 cm^{-1} and that of fluorescence band is 1,600 cm^{-1}. The absorption spectra of **1** in aqueous micelles show an unresolved two-band structure, having band maxima at ~325 and 340 nm, with relatively narrowed FWHM (~2,800 cm^{-1}). Similar to that in Aerosol OT, a sharp fluorescence band (FWHM of ~900 cm^{-1}) is noticed. This indicates the existence of inhomogeneous segments[1,2] of poly(dimethylsilylene) backbone in micelles, and the emission originates from an adiabatically formed longest segment.[1,2] The segment length of poly(silylene) is considerably increased in aqueous micelles when compared to that in Aerosol OT and that explains the observed red shift in the absorption and fluorescence bands. The segment behavior is also reflected in the fluorescence quantum yields.[9] In Aerosol OT with high inhomogeneity in the segment lengths, and an expected efficient energy transfer process between the segments, the observed fluorescence quantum yield is considerably low; whereas in aqueous micelles, the segment lengths are almost similar and exhibit near unit fluorescence intensities (Table 1).

The difference in spectral properties of **1** in aqueous and non-aqueous micelles can be understood by considering the micelle structure and poly(silylene) binding location in the micelle. Because of its hydrophobic nature, poly(silylene) **1** prefers to stay at the interface of Aerosol OT reverse micelles, which is relatively loose and incapable of enforcing any conformational change in the poly(silylene) backbone. On the other hand, in aqueous micelles, as **1** prefers to stay in the tightly held hydrophobic micelle core region, drastic micelle induced conformational changes in the backbone are expected. However, considering the dimensions of micelles and **1**, polymer **1** might be encompassed by a few micelles instead of one. If that is not the case, because of insufficient micelle diameter, the polymer should take a coiled structure to wrap by a single micelle. As the spectral properties in aqueous micelles can only explained assuming an elongated *transoid* backbone conformation of **1**, encapsulation of the entire poly(silylene) backbone by a single spherical micelle is impossible. But that could be expected when the micelle has a wormlike structure. However, the following reasons support the concept of **1** being wrapped by three spherical micelles instead of a single wormlike micelle.

To understand the micelle structure in the presence of **1**, we have studied the spectral properties of **1** in three anionic surfactants, SDES, SDS and SHS, having same head group but different alkyl chain lengths. The diameters of the spherical micelles formed with SDES, SDS and SHS surfactants are ~2.0, 2.5 and 3.5 nm, respectively, and the corresponding full length of all-*anti* poly(dimethylsilylene) is ~6.7 nm.[11] The absorption spectrum of **1** shows the micelle size dependent band maximum: the band maximum of **1** in SDES and SDS is 340 nm whereas that in the relatively larger micelles of SHS is 324 nm (Figure 1a). Because of suitable micelle size *versus* length of **1**, three spherical micelles of SDES/SDS having ≤2.5 nm diameter can be easily accommodated on the poly(dimethylsilylene) backbone, whereas SHS micelles with a relatively bigger micelle size cannot. In the SHS case, only two micelles can encompass a major part of the poly(silylene) backbone and the remaining part becomes a pendent moiety and kinks formation could be expected, giving rise to a blue shifted absorption band. On the other hand, if a single wormlike micelle that can overlap entire poly(silylene) backbone is assumed to form in solution, the absorption spectrum of **1** should not have shown a surfactant alkyl chain length dependent absorption spectrum.

To check the predictions made in the last paragraphs we have performed the micelle structural estimation in the presence of **1** and the effect of electrolytes and temperature on it. The polarity of the micelle core is known to depend on the aggregation number and micelle structure.[5,7a] The estimated polarity of the SDS micelles bound with **1** using pyrene as an extrinsic fluorescence probe is the same as that of the free SDS micelles,[12] indicating a similar aggregation number and spherical structure of the micelles in the presence of **1**. It is known that added electrolytes such as NaCl induce spherical-to-wormlike micelle structural change.[5] The absorption spectrum of **1** shows a marked dependence upon the micelle structural change. A new absorption band at 347 nm emerges with the addition of NaCl (0.5 M) to **1** in SDS at room temperature. This new band can be assigned for an all-*anti* poly(silylene) backbone encompassed by a wormlike micelle. Since, the micelle aggregation number and sizes are comparatively smaller at elevated temperatures,[5] the disappearance of the 347 nm band by increasing temperature and its re-emergence with decreasing temperature is in agreement with the above predictions.

In conclusion, we have reported herein for the first time, the absorption and fluorescence spectral features of compound **1** in several micelles. In reverse micelles, **1** has a random-coil structure, whereas in aqueous micelles, a micelle-induced rodlike backbone structure is preferably formed. The structural estimation of micelles reveals that three micelles having moderate size are encompassed on the poly(silylene) backbone to form a 1:3 poly(dimethylsilylene)-micelle complex, which is soluble in water. The effect of electrolytes and temperature on the spectral properties of **1** further emphasizes the role of the micelle structure on the poly(silylene) backbone conformation.

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9 Poly(dimethylsilylene) (Mw = 2,000, Waco Pure Chemicals) and surfactants [SDES, SDS, SHS and Aerosol OT (Aldrich)] were used as received. Naphthalene and anthracene [ϕ_f = 0.23 and 0.36 in cyclohexane, respectively (*Handbook of Fluorescence Spectra of Aromatic Compounds*, I. B. Berlman, Academic Press, New York, 1965)] were used as the reference compounds to estimate the fluorescence quantum yields of **1** in Aerosol OT and aqueous micelles, respectively.

10 The X-ray studies on perchloropoly(silylene) having a similar sized substituent chlorine, J. R. Koe, D. R. Powell, J. F. Buffy, S. Hayase and R. West, *Angew. Chem. Int. Ed.*, 1998, **37**, 1441 and permethyldecasilane, an oligomeric analogue of **1**, K. Sakamoto, T. Naruoka and M. Kira, unpublished results, indicates the all-*anti* backbone conformation of poly(silylene)s in the solid state. The measured absorption and fluorescence band maxima of **1** in solid KBr matrix, in which an all-*anti* backbone conformer of **1** is expected, are 349 and 357 nm, respectively, slightly red shifted from but consistent with the values found in aqueous micelles.

11 The diameter of the spherical micelle corresponds approximately to double the extended length of the alkyl chain of the surfactants. The lengths of all-*trans* alkyl chains and **1** are estimated from the energy minimized structures using PM3 calculations. A similar diameter of 2.5 nm is reported in the literature for SDS spherical micelles (Ref. 5).

12 The fluorescence intensity ratio of pyrene 0,0 and 0,2 bands (I_1/I_3) is same (1.0) in the presence and absence of **1** in SDS. A similar observation has been made in the literature (Ref. 7a).