Micellization coupled with facilitation of J-aggregation for poly(1,3-cyclohexadiene)-based amphiphilic block copolymers†

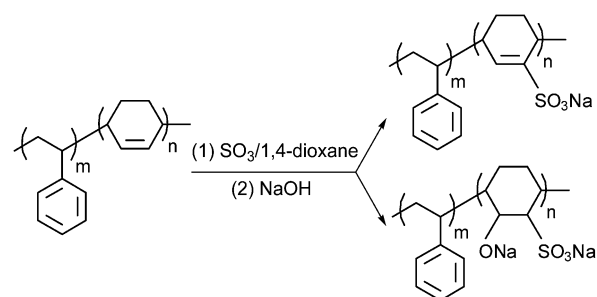Jiaping Lin,*[a] Weiwei Ding,[a] Kunlun Hong,*[b] Jimmy W. Mays,[bc] Zhongde Xu[a] and Yizhong Yuan[a]

Amphiphilic PS-b-sPCHD copolymers can associate to form micelles with PS blocks as the core surrounded by sPHCD blocks in aqueous media. J-Aggregation of the chromophores in sPCHD blocks is significantly facilitated by the micellization, resulting in a remarkable change in the photophysical properties of PS-b-sPCHD.

Self-assembly of amphiphilic block copolymers in selective solvents gives rise to micelle formation, with the insoluble blocks as the core and the soluble blocks as the corona. The nanoscale structures formed find a range of potential applications in catalysis, drug delivery, as photoelectric devices and as nanoscale reactors.[1] Many studies have been carried out on the self-assembly of block copolymers consisting of a hydrophobic block and a hydrophilic block. For example, in a series of papers, Eisenberg et al. reported the self-assembly behavior of amphiphilic polystyrene-based block copolymers (e.g., polystyrene-block-poly(acrylic acid) and polystyrene-block-poly(ethylene oxide)).[2] In aqueous media, polystyrene is the hydrophobic core-forming block, while poly(acrylic acid) and poly(ethylene oxide) are the hydrophilic corona-forming blocks. The influences of molecular structure, pH value, salt addition and preparation method have been investigated. However, so far most of the research on micellization has been limited to morphological studies of micelles. Relatively few studies on the micellization of block copolymers containing blocks with interesting photophysical and electronic properties have been reported. Jenekhe et al. have studied the self-assembly of copolymers with π-conjugated polymer blocks, such as poly(phenylquinoline) and poly(9,9-dihexylfluorene-2,7-diyl). It was found that the photophysical and electronic properties of the block copolymer varied with the supramolecular structure.[3] Self-assembly of these block copolymers provides an opportunity to generate functional materials with well-defined supramolecular architectures.[4]

Poly(1,3-cyclohexadiene) (PCHD) is a structurally interesting material. The alicyclic structure with C=C double bonds imparts many interesting photophysical, electronic, thermal and mechanical properties. Through post-polymerization chemistry, such as aromatization or hydrogenation, PCHD can be converted to other novel materials having unique properties.[5] The 1,3-CHD monomer is also able to copolymerize with other monomers, such as styrene, to form block copolymers.[6] Through sulfonation of PCHD (represented in Scheme 1), a novel PCHD-based amphiphilic copolymer can be obtained.[6d] In this work, three PS-b-sPCHD block copolymer samples (denoted as PS-b-sPCHD-1, PS-b-sPCHD-2 and PS-b-sPCHD-3) were synthesized,† and their characteristics are shown in Table 1. Self-assembly and its influence on the photophysical properties of these novel polystyrene-b-sulfonated PCHDs (PS-b-sPCHDs) were investigated using transmission electron microscopy (TEM), laser light scattering (LLS) techniques, and fluorescence spectroscopy. It was found that PS-b-sPCHDs can self-assemble to form micelles in aqueous media, which has a remarkable effect on their photophysical properties. The J-aggregation of the chromophores in the sPCHD blocks (which produces a red-shifted and narrow-banded absorption compared to the monomer absorption band[7]) was found to be significantly facilitated by the micellization.

Fig. 1 shows typical morphologies of micelles formed by PS-b-sPCHD. The micelles are spherical, and most of them have diameters in the range 30–60 nm. For the three block copolymers examined, variation in the sPCHD content had no effect on the morphologies

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† Electronic supplementary information (ESI) available: Synthesis and characterization of PS-b-sPCHD block copolymers, as well as details of the preparation and characterization of the micelle solutions. See DOI: 10.1039/b804838j
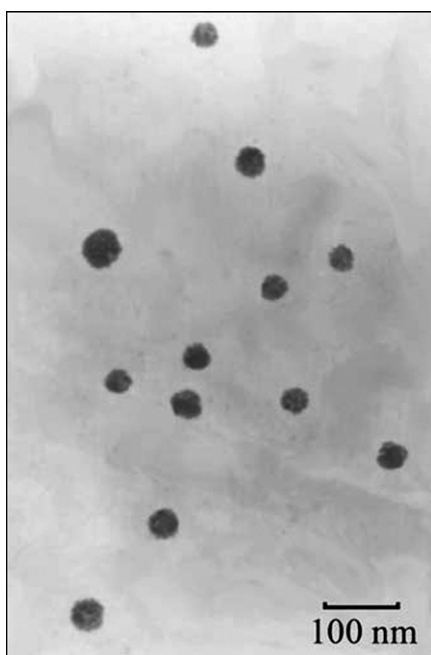

Scheme 1 Schematic representation of the sulfonation of PCHD.

Table 1 Characteristics of PS-b-sPCHD block copolymers

| Sample | PS-b-PCHD precursor | | | Degree of sulfonation (%) |
	PDI	M_n/kg mol^{-1}	PCHD content (wt %)	
PS-b-sPCHD-1	1.04	15.5	86.9	85.9
PS-b-sPCHD-2	1.03	15.3	57.1	83.2
PS-b-sPCHD-3	1.02	11.7	28.7	85.5

Fig. 1 TEM photograph of the micelles formed by PS-*b*-sPCHD-1.

formed; all the observed micelles were spherical. The micelle formation was also confirmed by laser light scattering experiments. In static LLS, a marked increase of excess scattering intensity from the PS-*b*-sPCHD aqueous solution was found when the polymer concentration was increased above a certain value for all the PS-*b*-sPCHD samples, which indicates that the PS-*b*-sPCHD copolymers aggregate and form micelles above a critical concentration. Fig. 2 shows a typical hydrodynamic radius $\langle R_h \rangle$ distribution for the micelles formed by PS-*b*-sPCHD-1. A narrow distribution of particle sizes was found. A plot of $\langle R_h \rangle$ against polymer concentration is presented in the inset of Fig. 2. It can be seen that the particle size, indicated by $\langle R_h \rangle$, is in the range 130–150 nm. This is larger than that obtained by TEM observation, as expected, since the TEM results are for dry micelles. For the micelles formed by the three PS-*b*-sPCHD samples, the difference in micelle size is less marked. It is also noted that the hydrodynamic radii of the micelles determined by LLS are larger than the contour lengths of the copolymer chains (*e.g.*, 85 nm for PS-*b*-sPCHD-1). The larger micelle sizes obtained by LLS can be reconciled with the building blocks if the polydispersity of the
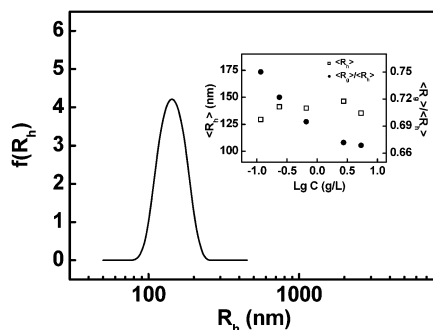
copolymer is taken into account. In addition, for LLS measurements, the micelles with hydrophilic corona chains are in a swollen state and the chains adopt an extended form. For the above reasons, the micelle sizes determined by LLS are consistent with the lengths of the copolymer chains.

The micelle structure can further be viewed in terms of the ratio of the average radius of gyration to the average hydrodynamic radius ($\langle R_g \rangle / \langle R_h \rangle$).[8] A plot of $\langle R_g \rangle / \langle R_h \rangle$ *versus* concentration is also shown in the inset. It is well known that the ratios of $\langle R_g \rangle / \langle R_h \rangle$ for a uniform nondraining sphere, a hyperbranched cluster, and a random coil are 0.734, ~1.0–1.3 and ~1.5–1.8, respectively.[8b,8c] The measured ratios of $\langle R_g \rangle / \langle R_h \rangle$ are in the range 0.66–0.80, indicating that the micelles are uniform nondraining spheres. Such light scattering results are in reasonable agreement with the TEM observations. It is also noted from the inset plot of Fig. 2 that the value of $\langle R_g \rangle / \langle R_h \rangle$ decreases with increasing polymer concentration. This implies that the micelles become more compact when polymer concentration increases.

Typical fluorescence excitation spectra of the PS-*b*-sPCHD solutions with various concentrations are shown in Fig. 3(a). At low concentrations, two peaks can be observed. The peak centered at longer wavelength is denoted as band 1, while the peak at shorter wavelength is band 2. On the formation of the micelles with increasing PS-*b*-sPCHD concentration, as evidenced by the TEM observations and LLS studies, the intensity of band 1 increases and band 2 becomes less noticeable with respect to band 1. Concomitantly with the change in the intensity, a significant red-shift of band 1 is demonstrated. The changes in the photophysical properties upon the micellization of PS-*b*-sPCHD exhibit characteristics of the J-aggregation phenomenon widely observed in dyes. When the dye molecules with π-electron chromophores are aligned parallel, two new excitonic bands are generated according to exciton theory, one with higher and the other with lower energy levels in comparison with
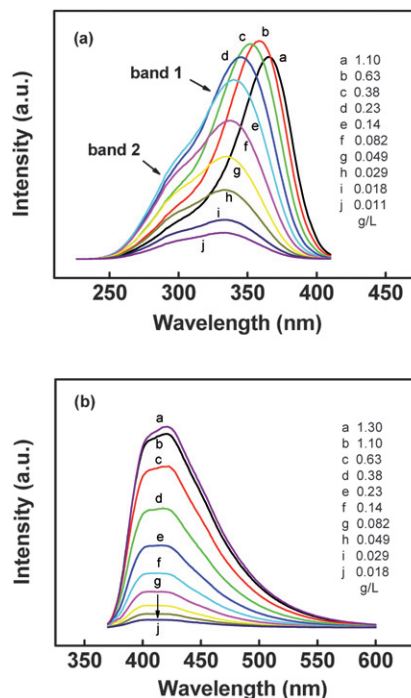

Fig. 2 Typical hydrodynamic radius distribution f(R_h) of PS-*b*-sPCHD-1 micelles in aqueous solution with polymer concentration of 4.3 g L^{-1} at 25 °C. Shown in inset are plots of $\langle R_h \rangle$ and $\langle R_g \rangle / \langle R_h \rangle$ versus concentration.

Fig. 3 Typical fluorescence excitation spectra (a) and emission spectra (b) of PS-*b*-sPCHD-2 in water at various copolymer concentrations.

the monomer energy level. In J-aggregates where the dislocation among the parallel molecules is larger, transition only to the low energy state of the exciton band is allowed. As a result, J-aggregation is characterized by an intense narrow absorption band that is red-shifted with respect to that of monomer molecules.[7,9]

For the PS-*b*-sPCHD, the fluorescence properties originate from the ethylenic π-electrons of the C=C bonds in the sPCHD blocks as shown in Scheme 1. The chromophores in the sPCHD blocks may form some J-aggregates in solution where the polymer concentration is below the critical micelle concentration. The J-aggregation could generate a red-shifted excitation band 1 with high quantum yields as shown in Fig. 3(a). The band 2 centered at 297 nm, which resembles the monomer band of PCHD in dilute THF solution,[5d] is taken as that of isolated chromophores. When the polymer concentration is increased, the micellization takes place. The hydrophobic PS blocks form the micelle cores and the hydrophilic sPCHD blocks containing the π-electron chromophores aggregate and form the coronas of the micelle, as schematically shown in Scheme 2. The semirigid chain nature of the sPCHD could cause the sPCHD blocks to be aligned parallel within the corona. As a result, the J-aggregation is significantly facilitated, giving rise to an intense band 1 of the aggregates. Meanwhile, band 1 also exhibits a red-shift with respect to band 2 of the isolated chromophores. As can be seen from Fig. 3(a), concomitantly with the progressive increase in the polymer concentration, the band 1 gradually shifts to longer wavelengths and its intensity increases. Such a phenomenon is in accordance with the fact that the spherical micelles become more compact with increasing polymer concentration (shown by the inset plot of Fig. 2). The compact structure of the micelles could give rise to an increased order of the sPCHD block alignments in the micelle corona. Since the order structure could facilitate the J-aggregation,[9d] an incremental red-shift accompanied with increase in peak intensity is shown for the band 1 when polymer concentration is progressively increased.

The corresponding emission spectra of PS-*b*-sPCHD solutions are given in Fig. 3(b). Two emission peaks, centered at 400 nm and 423 nm, are observed for low polymer concentration solutions. With increasing polymer concentration, the intensities of both peaks increase. However, the emission peak at longer wavelength, which is attributed to the J-aggregates, becomes stronger with respect to that at shorter wavelength (attributed to the isolated chromophores). The J-aggregate peak also shows a slight red-shift as the polymer concentration is increased.

More information regarding the relationship between the copolymer micelle formation and its photophysical properties is provided in Fig. 4, in which plots of the intensity ratio of band 1 to band 2 (I_1/I_2)
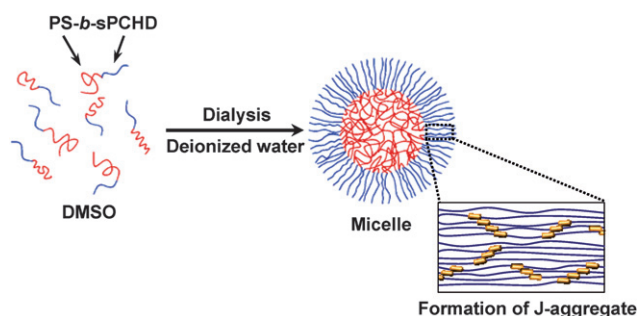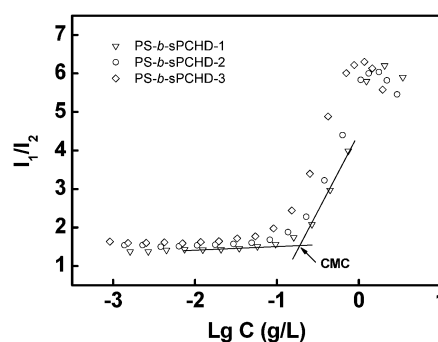

Fig. 4 Plot of the intensity ratio of I_1/I_2 of excitation spectra as a function of concentration.

of excitation spectra against the concentration are shown for the three block copolymer samples. For low concentrations of PS-*b*-sPCHD, negligible changes in the magnitude of the intensity ratio are observed. But as the polymer concentration increases, the value of the ratio increases dramatically at a certain concentration in a sigmoidal manner. The deviation from linearity for the intensity ratio in Fig. 4 generally corresponds to the onset of micellization as evidenced by the laser light scattering studies and TEM observations. In the present work, we designated the intersection point (shown in Fig. 4) of the tangent to the curve at the inflection with the horizontal tangent through the points at low polymer concentrations of I_1/I_2 curve as the critical micelle concentration (CMC). The determined CMC values are 0.18 g L^{-1}, 0.12 g L^{-1}, and 0.087 g L^{-1} for PS-*b*-sPCHD-1, PS-*b*-sPCHD-2, and PS-*b*-sPCHD-3 with sPCHD contents of 86.9 wt%, 57.1 wt%, and 28.7 wt%, respectively. The CMC value tends to decrease with decreasing content of sPCHD in the block copolymer, suggesting that the self-assembly tendency of the PS-*b*-sPCHD sample increases. This is expected, since with decreasing sPCHD content, the hydrophobicity of the sample becomes greater. As a result, the CMC value decreases. It is noted that aggregation observed by the LLS appears at a relative lower concentration than the CMC value determined by the fluorescence spectra. This can be explained if the micellization takes place gradually due to the polydispersity of the block copolymers. In addition, from Fig. 4, it can be seen that the value of I_1/I_2 starts to increase at relative lower concentration than the defined CMC. This indicates that weak aggregation takes place at lower concentration. Such an aggregation can be detected by LLS.

In summary, the micellization behavior of novel amphiphilic block copolymers of PS-*b*-sPCHD was studied. The amphiphilic block copolymers were found to associate to form polymeric micelles in aqueous media. Fluorescence spectroscopy studies suggest that the photophysical properties of the PS-*b*-sPCHD change substantially in the micellization due to the facilitation of J-aggregation of the chromophores in sPCHD blocks. This allows for the determination of the critical micelle concentration. Aggregates of dyes have been extensively studied and are known to have novel cooperative optical and nonlinear optical properties. However, very little is known about J-aggregation of polymers. The present results provide evidence of J-aggregation in the self-assembly of block copolymers. The self-assembled PS-*b*-sPCHD micelles may find useful applications as building materials in intelligent environment-responsive nano-engineering.[10] For example, the development of blue-emitters is critical for generating lights of different colors (including white light)

Scheme 2 Schematic representation of the micellization of PS-*b*-sPCHD and formation of J-aggregation.

for OLED (organic light-emitting diode) applications.[10d] PS-*b*-sPCHD aggregates with a blue-emitting nature could act as the active blue-emitting material for OLED devices, and the properties of the device could be manipulated by copolymer composition. In addition, the nature of the PS and sPCHD blocks could have effects on the self-association. For example, changes in pH value and temperature could influence the chain conformation of the polyelectrolyte sPCHD, and thus the self-assembly. Therefore, the photophysical properties may also be manipulated by the self-assembled structures, and this will be examined in further work.

Acknowledgements

Notes and references

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