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Nanosized Micelles Formed by the Self-assembly of Amphiphilic Block Copolymers with Luminescent Rhenium Complexes

Sijian Hou, Ka Yan Kitty Man, and Wai Kin Chan*

Department of Chemistry, University of Hong Kong, Pokfulam Road, Hong Kong, China

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We have synthesized a series of polystyrene-*block*-poly(4-vinylpyridine)s (PS-*b*-PVP) to which luminescent tricarbonyl(2,2′-bipyridyl)rhenium(I) complexes were attached. The rhenium complexes could induce the self-assembly of the copolymers into nanosized micelles with different shapes and dimensions, depending on the block size distribution of the copolymers and the solvent system being used. In general, spherical micelles were observed when methanol, a nonsolvent for the polystyrene block, was added to a copolymer solution in dichloromethane. Micellization was observed when the added methanol concentration was approximately 30%. When toluene, a nonsolvent for the poly(4-vinylpyridine) block, was added to the copolymer solution in dichloromethane, micelles with different interesting shapes were observed. For copolymers with larger PVP block size, spherical micelles were observed. When the relative block size of the PVP block was reduced, the micelles gradually changed to disk or vesicle structures and then to rodlike structures. The rhenium complex can act as a luminescent probe in the resulting nanosized micelles and provide sufficient contrast for electron microscopic studies. Significant changes in luminescence spectra were observed after the micellization.

Introduction

During the past decade, interest in the preparation of nanosized aggregates from highly asymmetric amphiphilic block copolymers has greatly increased.[1,2] Block copolymers play an important role in the preparation of nanosized polymer aggregates or particles due to their well-defined structural and morphological behavior.[3] There have been several examples of self-assembly of amphiphilic block copolymers in specific solvent systems. Eisenberg et al. synthesized a series of amphiphilic block copolymers that consisted of a nonpolar polystyrene block and a polar block such as poly(acrylic acid),[4] poly(ethylene oxide),[5] or an ionomer.[6] Interesting "crew-cut" aggregates were observed in these polymers, and the effect of metal ions on the morphology of the aggregates was also studied.[7] The formation of cylindrical micelles from polystyrene-*block*-poly(4-hydroxystyrene) induced by self-hydrogen-bonding was reported by Pearce et al.[8] In another example, Liu et al. reported the formation of nanospheres by polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) in which the cinnamoyl groups could undergo subsequent photo cross-linking.[9] More recently, Manners reported the self-assembly of poly(ferrocene) block copolymers into cylindrical micelles.[10] After being exposed to capillary forces, "ceramic lines" can be generated by subsequent reactive ion etching.[11] The polymer aggregates were prepared by dissolving copolymers in a common solvent for both blocks, followed by the addition of a poor solvent for one block. The shapes of the micelles depend on the chemical nature of the copolymers, solvent systems, and preparation procedures. In general, the solubility difference between different blocks makes one block expand and the other condense. The driving force for micellization in such systems is the repulsive interactions between one of the blocks and the solvent. Spherical structures are observed frequently because of the preference in free energy. In some cases, disklike and rodlike structures were also observed.

Antonietti has reported the micellization of PS-*b*-PVP in selective solvents.[12] In our previous papers, we extended this work by synthesizing a series of polystyrene-*block*-poly(4-vinylpyridine)s (PS-*b*-PVP) that were incorporated with rhenium tricarbonyl diimine complexes.[13] Luminescent d^6 transition-metal complexes have been demonstrated to be useful probes of molecular structures[14] and heterogeneous media,[15] as well as photosensitizers for solar energy conversion[16] and electron-transfer reactions.[17] It

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* To whom correspondence should be addressed. E-mail: waichan@hkucc.hku.hk.

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has been previously demonstrated that these molecular or polymeric transition metal complexes can play different roles in the optoelectronic processes including photosensitizers,[18] charge transport species,[19] and light emitting groups.[20] Their photophysical properties have also been studied extensively.[21,22] In designing our rhenium-containing block copolymers, it was expected that the rhenium complexes can serve different functions. First, since the metal complex is ionic in nature, the rhenium-functionalized PVP block could induce the self-assembly of the block copolymers into different forms of micelles. Second, the emissive complexes tagged on the block copolymers can act as luminescent probes in the resulting micelles.[23] This allows us to study the interaction of these particles in different environments, since the luminescence properties are strongly dependent on the medium.[24] Finally, the heavy rhenium atom can provide sufficient contrast in electron microscopic studies, which could facilitate a study of the nanostructures formed by the copolymers. We have found that by varying the relative sizes of the PS and PVP blocks and the solvent, micelles with different interesting morphologies could be obtained.

Experimental Section

Materials. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketal. It was dried in a flask coated with sodium mirror prior to use. Styrene and 4-vinylpyridine were purchased from Lancaster Synthesis Inc. Silver perchlorate and rhenium pentacarbonyl chloride were purchased from Strem Chemical Inc. and were used as received. Chlorotricarbonyl(2,2′-bipyridyl)-rhenium(I) was synthesized according to the literature procedure.[25] All solvents used for light scattering studies were HPLC grade and were filtered through a nylon membrane filter (0.2 μm) prior to the experiment.

Instruments. ^{1}H NMR spectra were collected on a Bruker 300 DPX NMR spectrometer. FTIR and UV−vis absorption spectra were collected on a BIO-RAD FTS-7 and Hewlett-Packard 8425A spectrometers, respectively. The emission spectra were collected on an ORIEL MS257 monochromator equipped with an ANDOR DV420-BV charge coupled device detector or on a Perkin-Elmer LS-50B spectrofluorometer. Molecular weight and distribution was determined by a GPC system equipped with an ISCO 2350 pump, ISCO V4 UV−vis absorbance detector, Viscotek 250 viscosity/refractive index dual detector, and two Ultrastyragel columns at 35 °C. THF was used as the eluent at a flow rate of 1 mL/min. The molecular weight was calculated based on polystyrene standards. Transmission electron micrographs were recorded on a JEOL-100 electron microscope operated at 80 kV. Light scattering studies were performed on a Wyatt Technology DAWN-DSP multiangle laser photometer with a He−Ne laser (632.8 nm). HPLC grade solvents were filtered with 0.2-μm nylon membrane filters. The vials for measurements were rinsed 3 times with methanol and dried in a dust-free environment.

Synthesis. Polystyrene-*block*-poly(4-vinylpyridine). PS-*b*-PVP was synthesized by anionic polymerization under high vacuum (10^{-6} mbar) using *sec*-butyllithium as the initiator and THF as the solvent.[26] Four copolymers with different styrene/4-vinylpyridine block size ratios were prepared. The number-average molecular weight ranged from 18 700 to 53 900 and their polydispersities were approximately 1.05−1.20.

Synthesis of Block Copolymers Functionalized with Rhenium Complexes. The syntheses of PS-*b*-PVP copolymers **A**−**D** were carried out by the reaction between (2,2′-bipyridyl)-rhenium(I) tricarbonyl chloride and the copolymer in the presence of silver perchlorate as described in our previously published procedure. (**Caution!** *Perchlorate salts are potentially explosive and should be handled with great care and in small amounts.*)

Preparation of Polymer Micelles. The rhenium-containing block copolymer was dissolved in distilled CH_2Cl_2 (concentration = 1 mg/mL) and filtered through a PTFE membrane filter (0.2-μm pore size). The second solvent was added slowly to the stirred polymer solution via a syringe pump at a constant rate. Typical addition rate was 1 to 5 mL/h. To estimate the ideal solvent composition for the formation of micelles, during the first trial, addition of solvent was continued until the solution turned turbid. In subsequent experiments, addition was stopped before the appearance of turbidity. The radii of gyration of the micelles were monitored by light scattering photometer. Stirring of solution was continued for 2 days before further characterizations.

Results and Discussion

Synthesis and Characterizations of Block Copolymers Functionalized with Rhenium Complexes. The functionalization of the poly(4-vinylpyridine) block was carried out by a modified procedure in a one-pot reaction (Scheme 1). For molecular rhenium complexes reported in the literature, a silver salt is usually required in order to activate the rhenium complex by removing the chloride ion. However, neither silver trifluoromethanesulfonate nor silver hexafluorophosphate gave satisfactory results. The degree of functionalization was very poor (<3%). We found that silver perchlorate gave the best results and approximately 20−40% of the vinyl pyridine unit was functionalized. The size and the solubility of the anion in organic solvents may be critical to the complexation reaction. The degree of functionalization was calculated by the NMR spectrum that showed the extra signals of the pyridinium moiety. After the complexation reaction, new peaks at 8.8−9.2 and 7.8−7.9 ppm appeared, which corresponded to the protons of the bipyridyl moieties and the protons on the pyridine rings that were coordinated with rhenium. The chemical shifts of these ad-

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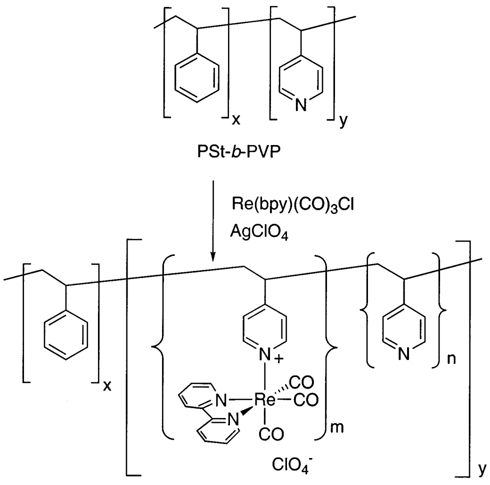
Scheme 1



polymer	y/x
A	3.1
B	1.3
C	0.72
D	0.35

ditional peaks are consistent with the spectral data of the rhenium pyridinium complexes reported in the literature.[25,27] The presence of the rhenium tricarbonyl moiety was also confirmed by FTIR spectroscopy. Three very strong stretching bands were found at 1922, 2020, and 2030 cm^{-1}, which are consistent to the *facial* CO stretching of the metal carbonyls. It should also be noted that the rhenium complexes were attached randomly within the PVP block, which may lead to an uneven distribution of metal along the polymer chain.

From the DSC thermograms of the copolymers, the glass transition temperature of the first PS block is 92 °C, while the metal-free copolymer **A** exhibits two distinct T_g at 96 and 144 °C. These results agree with those reported in the literature.[28] After functionalization with the rhenium complex, the T_g of the PVP block shifted to 170 °C, while that of the PS block did not show significant change. The increase in the glass transition temperature indicates a stronger interaction between the ionic polymer chains. This further supports the formation of two distinct block structures in the copolymer molecules.

The metal-free copolymers do not absorb in the visible region. However, after being incorporated with the rhenium complex, their electronic absorption and emission behavior changed significantly. The UV−vis absorption and luminescence spectra of copolymer **D** in dichloromethane (DCM) are shown in Figure 1. The absorption band at ca. 300 nm is assigned to the intraligand $\pi-\pi^*$ transition of the bipyridine moiety. The absorption band due to the MLCT transitions ($d-\pi^*$) is clearly observed as a shoulder at ca. 380 nm and the tail extends beyond 400 nm. This characteristic rhenium complex electronic excited state is also revealed by its luminescent spectrum. Excitation at 350 nm gave rise to an intense emission band centered at 530 nm. This is attributed to the emission from the MLCT states of the rhenium bipyridyl complex. Other copolymers exhibit similar electronic transition behavior in DCM solution.

Solvent-Cast Films of the Copolymers. The morphologies of the copolymer films were studied by transmission electron microscopy (TEM). When taking photos, the polymer films were not stained with any chemicals, and the contrast of the image in the TEM photos can only originate from the rhenium complexes incorporated into the copolymers. In the solid phase, the ionic rhenium complexes aggregate and form isolated nanodomains that are dispersed in a polystyrene matrix. The dimensions of the domains are in the range between 20 and 100 nm and are mainly spherical in shape. Annealing of the film near the glass-transition temperature gave no significant improvement in the image contrast.

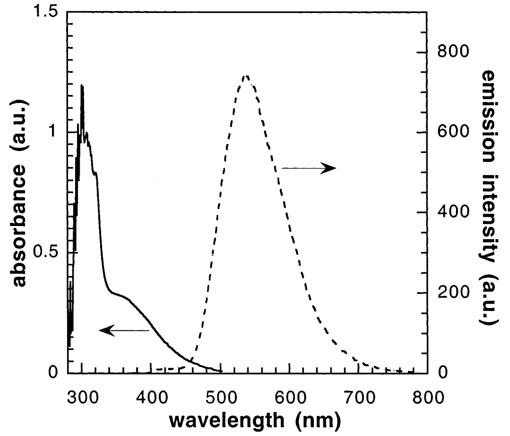


Figure 1. UV−vis absorption and emission spectra of copolymer **D** in dichloromethane.

Self-assembly of Block Copolymers into Micelles. Due to the different nature between the PS and the rhenium functionalized PVP blocks, the copolymers could undergo self-assembly into nanosized micelles induced by the selective solvent systems. By this process, different nanostructures with various shapes and dimensions can be obtained. As a general procedure, the block copolymer under study was dissolved in a good solvent for both blocks with a typical concentration of 1 mg/mL. A second solvent, which is a poor solvent for one of the blocks, was then added to the polymer solution very slowly. The dimensions and shapes of the resulting polymer micelles were studied by various techniques including laser light scattering and transmission electron microscopy. We chose different solvent systems to study the effect. In the methanol−dichloromethane (MeOH−DCM) solvent system, methanol was slowly added to a DCM solution of the copolymers. Since methanol is a poor solvent for PS, the PS block condensed gradually and the PVP block constituted the outer shell of the particles. Like in the solid samples, the rhenium atoms could provide sufficient contrast to the electron micrographs. The TEM micrographs of copolymers **A**−**D** formed in MeOH−DCM system are shown in Figure 2. All the functionalized copolymers with different block sizes formed spherical micelles. Among the four copolymers, the diameters of the spherical micelles are in the range between 20 and 100 nm, except for copolymer **D,** which forms spherical micelles with a diameter of approximately 300−400 nm. It should be noted that the dimensions of these micelles are considerably larger than the full stretch length of the polymers. Therefore, it is likely that the micelles contain more than one layer of polymers. The formation of multilayer structures may be due to the rapid change in solvent composition upon addition of the poor solvent. Adding the solvent at a slower rate (<0.1 mL/h) gave no significant difference. We also tried to change the solvent composition by diffusing the poor solvent into the polymer solution. However, it took a very long time and the change in solvent composition gave unreliable results. The very high contrast in the

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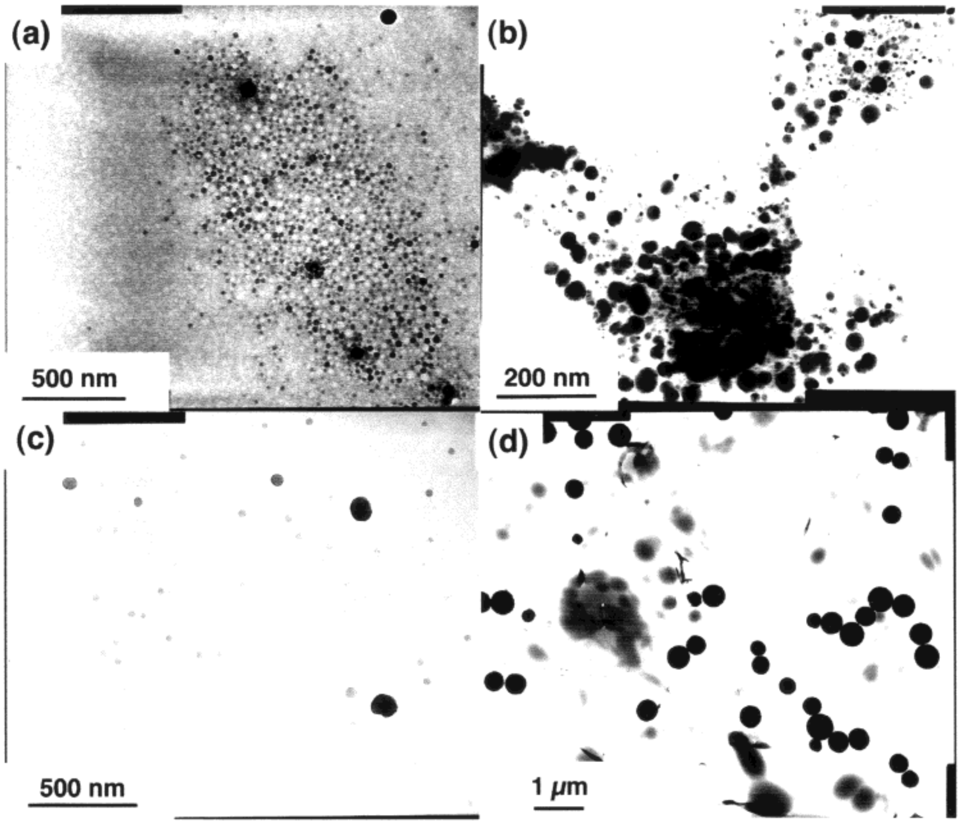

Figure 2. Transmission electron micrographs of the micelles formed by (a) copolymer **A,** (b) copolymer **B,** (c) copolymer **C,** and (d) copolymer **D** in the methanol−dichloromethane system (See ref 12).

Table 1. Properties of the Rhenium Functionalized Diblock Copolymers

copolymer	y/x	$m/(m + n)^a$	$M_n{}^b$	PD^c
A	3.1	0.13	53 900	1.13
B	1.3	0.40	18 700	1.05
C	0.72	0.38	22 800	1.20
D	0.35	0.21	30 800	1.16

[a] Fraction of the poly(4-vinylpyridine) block that was functionalized with rhenium complexes. [b] Number-average molecular weight of the starting diblock copolymers determined by GPC. [c] Polydispersity.

Table 2. Summary on the Dimensions and Shapes of Micelles Formed by Copolymers A−D under Different Conditions

copolymer	solvent system	dimension and shape of micelles,[a] nm
A	MeOH−DCM	spherical, diameter = 40−160 nm
B	MeOH−DCM	spherical, diameter = 40−80 nm
C	MeOH−DCM	spherical, diameter = 40−100 nm
D	MeOH−DCM	spherical, diameter = 300−400 nm
A	toluene−DCM	disklike, diameter = 130−200 nm
C	toluene−DCM	spherical, diameter = 20−40 nm
D	toluene−DCM	rodlike, diameter ∼ 40 nm length = 150−700 nm
A	hexane−DCM	disklike, diameter = 130−250 nm
A	ethyl acetate−DCM	rodlike, diameter ∼ 80 nm length = 150−600 nm

[a] From TEM results.

micrographs also suggests that the shells of the micelles are composed of several layers of polymer molecules. Table 2 summarizes the dimension and shape of the micelles formed by the copolymers under different conditions.

Effect of Other Solvent Systems on the Structure of Micelles. The functionalized block copolymers are not pure diblock copolymers because the rhenium complexes are distributed randomly within the PVP block (vide supra). Therefore, they may exhibit far more complex microstructures than simple amphiphilic diblock copolymers, and the sizes and shapes of the micelles formed may be very sensitive to the solvent systems. The effect of the structure of the micelles in different solvent systems was studied. When a nonpolar solvent, such as toluene, was added to the copolymer solution in DCM, micelle formation was observed only for those copolymers with either relatively large PVP or PS block sizes. No micelle formation was observed in copolymer **B** whose polymer blocks have similar sizes. It was also observed that the shapes of the micelles varied according to the relative size of the PS/PVP blocks. For copolymer **A**, the particles appear to be spherical at lower magnification. However, at higher magnification, a core−shell structure was observed in its TEM photo (Figure 3), in which the central part of the micelles is more transmissive. Considering that the contrast of the image originates from the rhenium atoms, a real core−shell structure cannot exist, because the PVP block should constitute the inner part of the particles. We suggest that there are two possible structures: The first one is a disklike structure in which the PS block constitutes the central part of the disk. As a result, less intense images were observed. However, since toluene is also a good solvent for the PS block, it cannot be safely assumed that the PS block constituted the inner part of the aggregate. The second possible structure is vesicular aggregates in which the inner and outer surfaces are of the same type of polymer block.[2h,7] In the picture, some solid spheres also coexist with the aggregates. Since the spherical form is preferred and more stable, the conversion from disk/vesicle to spherical structures cannot be completely excluded.

Copolymer **C** exhibits the normal spherical features as in the case for the MeOH−DCM system. On the other hand, having the smallest PVP block size among the

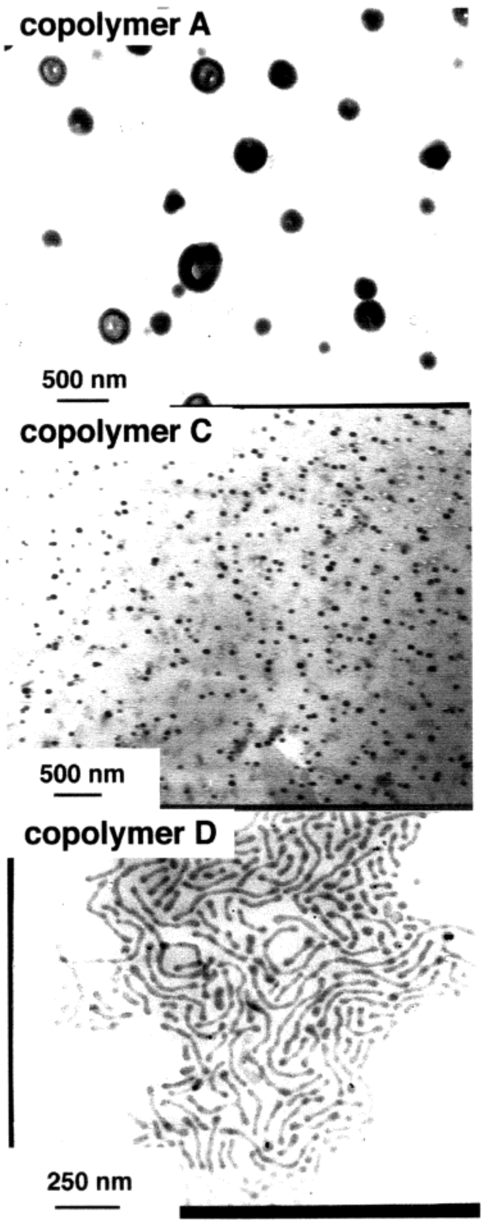

Figure 3. Transmission electron micrograph of the micelles formed by copolymers **A**, **C**, and **D** in toluene–dichloromethane.

copolymers, the micelles formed by copolymer **D** demonstrate very interesting structural features in the toluene–DCM system. Rodlike aggregates were observed when toluene was added to the DCM solution of the copolymer.[12] The diameter of the rod was approximately 40–50 nm, and the length varied in a very wide range between 100 and 700 nm (Figure 3). Like in other solvent systems, the diameter of the rod is also considerably larger than the dimension of a single polymer molecule, which is attributed to the formation of multilayer structures on the rod surfaces. Previous studies attributed the change in morphologies of aggregates to the presence of electrolytes.[7a] In our case, the change in solvent polarity may play a role in such changes in micelle structures.

It was found that copolymer **A** could exhibit different micelle structures in other solvent systems. When hexane was used as the nonpolar solvent and added to a DCM solution of copolymer **A**, a core–shell structure was observed (Figure 4). The aggregates in this solvent system did not show a significant difference in dimension and shape compared to the micelles obtained in toluene–DCM system. Again we suggest that disk and vesicle are the possible structures.

When a polar solvent was added to the copolymers dissolved in DCM. The structure of the micelles was different. The PVP block constituted the outer shell of the particles and the PS block condensed at the center. Figure 5 shows the TEM photo of the micelles obtained from the ethyl acetate–DCM solvent system. A branch rod structure was observed. From the contrast of the images, it can be seen that the branches are not coplanar. Such structural features are very similar to that of the previously reported amphiphilic block copolymer.[5]

Studies on the Formation of Micelles. The micellization processes were monitored by static light scattering. In a solvent system in which the two components are not isorefractive, the refractive index increment (dn/dc) value cannot be calculated and we can only estimate the rms radius of gyration (r_g) that was calculated based on the angular function of the scattered light intensity. The rms radius of gyration was measured as the second solvent was added to a polymer solution in DCM at a very slow rate. With the addition of the second solvent, the r_g value of the particles increased gradually until the concentration at which there is a sudden change in particle size. Figure 6 shows the change in r_g of copolymer **D** as the function of added methanol content in the solution. In the initial stage, the r_g value increased gradually, which corresponds to the successive formation of multilayer structures. When the added methanol fraction exceeded 30%, there is a sharp increase in the r_g value. It corresponds to the formation of "super aggregates" in which few micelles assembled to

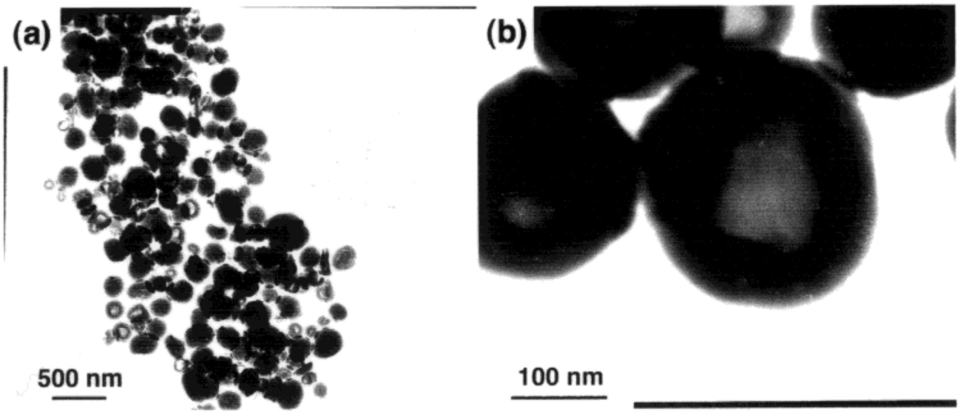

Figure 4. Transmission electron micrograph of the micelles formed by copolymer **A** in the hexane–dichloromethane system under different magnification.

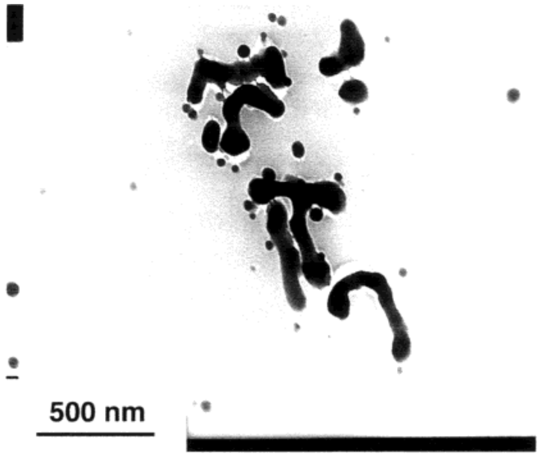

Figure 5. Transmission electron micrograph of the micelles formed by copolymer **A** in the ethyl acetate−dichloromethane system.

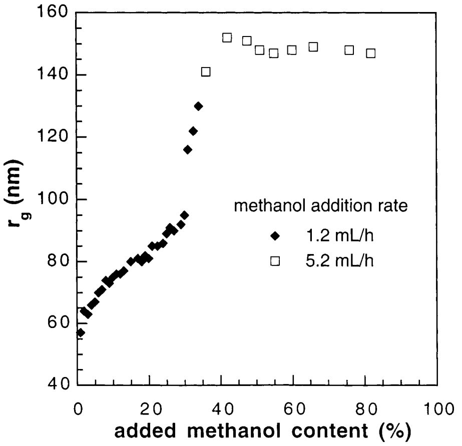

Figure 6. Plot of rms radius of gyration of copolymer **D** as the function of methanol content in the solution.

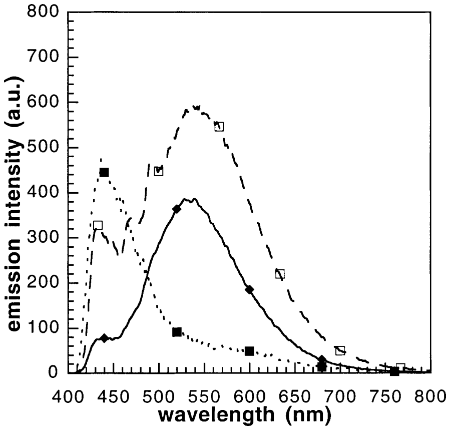

Figure 7. Solid-state emission spectra of copolymer **A** (◆) and copolymer **D** (□) and the emission spectrum of micelles formed by copolymer **D** in the MeOH−DCM system (■).

form bigger structures. The formation of such aggregates was also supported by the TEM pictures, which showed a high polydispersity in the sizes of aggregates. For the DCM−methanol solvent systems, most of the polymers underwent micelle formation with the methanol concentration of approximately 20−40%. For the DCM−toluene system, no formation of micelle was observed before the concentration of toluene was increased up to 70−80%. This is because addition of small amounts of toluene will not change significantly the polarity of the solvent.

Significant changes in the emission properties were observed after the formation of micelles. Figure 7 shows the luminescence of the nanosized micelles of copolymer **D** formed in the DCM−MeOH system. The solid-state emission spectra of copolymers **A** and **D** are also shown for comparison. In the solid state, all copolymers show an intense emission peak centered at ca. 540 nm, which shifted approximately 10 nm compared to the solution emission spectra (Figure 1). However, after micellization, the emission intensity decreased dramatically at this wavelength, and a new emission band developed at shorter wavelength. Such a shift in emission band is probably due to a lack of dipole reorganization resulting from the change in surrounding environment. Other quenching mechanisms may also play a role in this process. Nevertheless, this dramatic change in emission properties can also serve as a good indication of micelle formation.

Conclusion

The micelle formation behavior of some amphiphilic polystyrene-*block*-poly(4-vinylpyridine)s functionalized with rhenium complexes were studied. The rhenium complex may induce the formation of micelles, serve as the luminescence tag, and enhance the contrast of electron micrographs. Depending on the relative size of the two blocks and the solvent system, the copolymers could form nanosized micelles with different sizes and shapes. Spherical, disklike, and rodlike micelles were observed from transmission electron micrographs. After micellization, the luminescence properties of the copolymers also changed significantly. These nanomicelles may serve as potential luminescence probes for chemical/light sensing applications.

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Supporting Information Available: DSC thermograms of copolymer **A** before and after functionalization with rhenium complex; TEM micrograph of a solution-casted thin film of copolymer **D**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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