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Polymer Micelles from Poly(acrylic acid)-*graft*-polystyrene

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ABSTRACT: Micelles have been prepared from poly(acrylic acid)-*graft*-polystyrene by direct injection of a dioxane solution of the polymer into water containing various concentrations of NaCl. The size of the final micelle depends on the polymer concentration in the dioxane solution and the ionic strength of the aqueous phase. A relatively weak dependence of the micelle size on grafting density has been found. TEM images of these micelles reveal a unique "multicore" structure in which small spheres (presumably polystyrene) are associated with intervening polyacid chains that provide the aqueous solubility. It has been found that a very hydrophobic molecule (pyrene) can be solubilized efficiently in water by dissolving it with the polymer in dioxane prior to injection into the water phase. The morphology of the micelles containing pyrene is spherical, according to TEM.

Introduction

The association of amphiphilic macromolecules has been the subject of research for several decades. It is well-known that block or graft copolymers have the potential to form micelles in selective solvents, i.e., solvents that are good for one of the blocks and a nonsolvent for the other.[1] Polymer micelles are of interest because of their structure−property relations[2] and their potential applications as solubilizers[3] and drug carriers.[4] It has been fairly well understood that structural and thermodynamic parameters such as critical micelle concentration (CMC), the association number of the copolymers in the micelles, and the size of the micelles depend on the selectivity of the solvents, the temperature, the molecular weight of the copolymer, the length of the blocks, and the sequence of the blocks.[5]

Relatively fewer studies concerning the micellization of graft copolymers have been carried out.[6] Most of the graft copolymer systems are studied in the solvents that are good for the grafts, which means the micelles can be described as cores consisting of lyophobic backbones surrounded by coronas composed of lyophilic grafts. Micelles in which the cores are composed of lyophobic grafts while the outer shells are made up of the lyophilic polymer backbones have not received much attention. Grosnell et al. determined the intrinsic viscosity as a function of solvent for graft copolymers of styrene and 2-vinylpyridine with both components used as backbones or grafts.[7] Tuzar et al. studied the association behavior of polyisoprene-*graft*-polystyrene in solvent mixtures selective either for the polyisoprene backbone or for the polystyrene grafts using light scattering and sedimentation techniques.[6f] Watanabe and Matsuda characterized the micelle formation of polystyrene-*graft*-poly(methyl methacrylate) copolymer in mixed solvents of THF and acetonitrile using emission probes.[8] More recently, Kikuchi and Nose reported the micelle formation and structure of poly(methyl methacrylate)-*graft*-polystyrene in a solvent mixture of acetonitrile/acetic acid ethyl ether with light scattering techniques.[9]

In this study we report the micelle formation of poly(acrylic acid)-*graft*-polystyrene copolymers in aqueous solution. Five graft copolymers with different degrees of grafting density were synthesized. The grafting reaction was achieved by reacting an amino-terminated polystyrene with poly(acrylic acid) activated by 1,3-dicyclohexylcarbodiimide to promote amide formation. The polymers were characterized by GPC and NMR spectroscopy. Micelles form readily on adding a dioxane solution of the graft copolymer directly to aqueous solution. The effects of grafting density of the polymers, the concentration of the copolymer solution in dioxane, and the ionic strength of the aqueous solutions on the micelle formation were studied. The solubilization of pyrene with the micelles was also examined.

Experimental Section

Polymer Backbone Synthesis. The backbone of the graft copolymer, poly(acrylic acid) was synthesized by free radical polymerization. An 8.30 g sample of acrylic acid (Aldrich; vacuum distilled prior to use) and 110 mg of AIBN freshly recrystallized from ethanol were dissolved in 60 mL of dioxane. The solution was transferred to a glass ampule and degassed by three cycles of freeze−pump−thaw at 3×10^{-2} Torr. The ampule was sealed under vacuum. Polymerization was carried out at 65 °C for 8 h. The polymer was recovered by adding benzene to the solution and then purified by repeated reprecipitation from dioxane with benzene as the precipitant. The last precipitate was dissolved in dioxane and freeze-dried. This polymer is denoted as PAA. A portion of the polymer was methylated with diazomethane and then characterized with gel permeation chromatography (GPC). The M_n of the PAA is calculated to be 2.0×10^4 (relative to PS standards). The polydispersity (M_w/M_n) was determined to be 1.4.

Preparation of Graft Polymer. An amino-terminated polystyrene ($PS-NH_2$) was synthesized by anionic polymerization techniques using cumyl potassium as an initiator.[10] The amino termination was accomplished with the help of a protected amino functionality, 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane.[11] The polymer was precipitated by addition to 60:40 methanol−water. The silyl protecting group was removed during the precipitation step. A portion of the amino-terminated polystyrene was then reacted with excess of 2-naphthoyl chloride in dry benzene at 25 °C for 3 h and was recovered by precipitation with methanol. The naphthalene moiety provides a convenient UV marker in the 320−340 nm region that is distinct from the polystyrene. GPC was used to estimate the molecular weight of the amino-terminated polystyrene as 2700 with a polydispersity of 1.1. This polymer is denoted as PS in the following discussions.

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Table 1. Graft Copolymer Composition As Determined by NMR and GPC Experiments

copolymer	PS wt % (NMR)	grafting density (mole %)[a]	MW$_n$ of polymer NMR[b]	MW$_n$ of polymer GPC[c] (PD)
G1	37.5	1.6	32 000	32 500 (2.00)
G2	63.3	4.6	54 500	50 900 (1.61)
G3	75.2	8.1	80 750	72 000 (1.63)
G4	78.1	9.5	91 250	81 700 (1.61)
G5	79.1	10.1	95 750	91 800 (1.51)

[a] Grafting density is defined as the mole percent of the −COOH groups coupled with PS on the PAA main chain and was obtained from NMR spectrum of polymer. [b] Molecular weights from NMR are calculated as the sum of the molecular weight of PAA chain (20 000) and the weight of PS chains as derived from grafting density. [c] Based on GPC and polystyrene standards. PD = (MW$_m$/MW$_n$).

Table 2. Light Scattering Data[a]

concn[b] (mg/mL)	MW$_{mic}$ × 10^{-8} [c]	R_g (nm)[c]	d_h (nm)[d] (μ_2/Γ)	ρ[e]	N_{agg}[f]
6.6	9.15	133	126.8 ± 0.7 (0.14)	2.10	9560
4.4	2.20	65.5	100.5 ± 1.2 (0.12)	1.30	2300
3.3	0.783	33.7	87.3 ± 1.1 (0.12)	0.772	818
1.7	0.365	37.5	45.0 ± 0.2 (0.10)	1.67	381
0.66			38.6 ± 0.3 (0.28)		

[a] Micelles were made by adding 0.5 mL of a G5 dioxane solution to 5 mL of a 1 mM NaCl aqueous solution. The micelles were then dialyzed against 0.025 M borax/HNO_3 (pH = 8.12) buffer solution for light scattering measurement. [b] The concentration of the dioxane solution injected into water as part of the micelle preparation. At a concentration higher than 6.6 mg/mL a precipitate formed. [c] Based on a Zimm analysis of the static light scattering data (see text). [d] ± values indicate the standard deviation of at least three independent determinations of d_h based on the cumulant analysis of the correlation function. The value of μ_2/Γ is the typical polydispersity index for the QELS data. [e] R_g/R_h (see text). [f] N_{agg} = MW$_{mic}$/MW$_{PAA-g-PS}$, where the molecular weight derived from the NMR analysis is used.

GPC Measurements. GPC experiments were performed on a Waters system using four Waters μ-Styragel columns with pore sizes of 500, 10^3, 10^4, and 10^5 Å, respectively. THF was used as the eluting solvent at a flow rate of 1.5 mL/min. Calibration parameters were obtained using standard polystyrene samples. The detection system consists of a Waters model R401 differential refractive index detector and a Hewlett-Packard 1050 UV−vis diode array.

Grafting Reactions. 1,3-Dicyclohexylcarbodiimide (DCC; from Aldrich) was used to promote the grafting reaction. DCC was added to a solution of PAA and PS−NH_2 with a DCC/PS−NH_2 ratio of 1.1 in dioxane at 25 °C.[12] The hydrated DCC adduct, dicyclohexylurea, precipitated after about 0.5 h. The reaction was assumed to be complete after 3 h. The precipitate was filtered out. Because of the large difference in the molecular weight between the PAA backbone (2.0×10^4) and PS graft (2700), a dialysis membrane with molecular weight cutoff of 8000 was selected to purify the copolymers. It is expected that the graft copolymers will remain in the dialysis bag while unreacted PS or small molecule species will be removed, as was confirmed by GPC. The filtrate was dialyzed extensively against pure dioxane using a Spectra/Por 6 membrane (regenerated cellulose, Spectrum) with a nominal molecular weight cutoff of 8000. This served to remove any unreacted polystyrene chains and small molecules that might exist in the solution. The ratio of interior to exterior solution was 15/400 mL and there were at least four changes of the exterior solvent. The ratio of PAA to PS−NH_2 was varied to produce five distinct graft copolymers with different degrees of grafting density. We denote these polymers as PAA-*g*-PS. After extensive dialysis against dioxane solvent, the graft copolymer samples were freeze-dried. A portion of each copolymer was methylated with diazomethane so that it was suitable for NMR measurements and GPC analysis. Only one peak was observed in GPC chromatograms and it was distinct from unreacted methylated PAA or homopolystyrene chains. In Table 1 the graft copolymer compositions are presented. As will be discussed later, copolymer G5 will be the focus of our micelle studies. This degree of grafting appears to be the upper limit that we can achieve with our method.

NMR Measurements. Purified graft copolymers were methylated by addition of excess diazomethane ether solution to polymer solutions in benzene. After the reaction was complete, the excess diazomethane and ether were allowed to evaporate and the benzene was removed by freeze-drying. The final methylated graft copolymers were dissolved in deuterated acetone. Proton NMR spectra were measured at 300 MHz on a Varian Unity Plus 300. The integrated NMR spectra were used to calculate the ratio of aromatic protons to the aliphatic protons of the methyl groups. The percentage of −COOH groups reacted with PS−NH_2 on the PAA backbone was calculated from the NMR data. Given the estimated molecular weight of the PAA backbone, this provided an estimate of the copolymer molecular weight. Fortuitiously, these values agreed rather well with estimates based on GPC elution curves using PS standards (see Table 1). The polydispersities of the graft copolymers are only slightly higher than that of the PAA backbone except for sample G1.

Micelle Preparation. Micelle solutions were prepared by adding graft copolymer solutions in dioxane dropwise to a mildly stirred aqueous solution that contained different concentrations of NaCl. The micelle solutions were then dialyzed twice against aqueous NaCl solution of the same concentration used in the preparation to remove the small amount of dioxane from the solution. As will be discussed later, the concentration of the polymer in dioxane influences the size of the micelle that is formed, as does the ionic strength of the aqueous solution. Spectacular changes in aggregate morphology as a function of preparation conditions have been reported by the Eisenberg group for polystyrene-*block*-poly(acrylic acid) "crew-cut" micelles.[13] These workers use a "reverse" procedure for micelle preparation relative to our method; that is, they add the precipitating solvent (aqueous salt, acid, or base) slowly to a solution of polymer in a solvent good for both blocks (DMF). This permits some degree of micelle equilibration during preparation because the polystyrene cores are highly swollen. Our micelles clearly are controlled primarily by the kinetics of aggregation. It is interesting to consider the time scale required for polymer−polymer collisions. For the micelles formed from polymer G5 the concentration of polymer in dioxane varied from 6.6 to 0.66 mg/mL (see Table 2), which corresponds to a molar concentration of polymer chains of 6.9×10^{-5} or 6.9×10^{-6} M. The diffusion-limited second-order rate constant in water at 25 °C is 7.9×10^9 M^{-1} s^{-1}.[14] Treating the polymer−polymer collision as a classical second-order reaction, the time between collisions is $(k_{diff}[\text{polymer}])^{-1}$, which ranges from 2 to 20 μs for the concentrations given above (this neglects the dilution when the dioxane is added to water). Therefore as the dioxane and water mix, and the PS chains collapse, the question is, do the PS chains collapse into glassy intrapolymer aggregates before interpolymer collisions, or is the PS collapse and interpolymer collision occurring on similar time scales? We believe the latter situation describes our experimental condition, but to prove this point we would have to study much more dilute stock dioxane solutions to ensure that all intracoil processes are complete before polymer−polymer collisions occur.

Quasi-Elastic Light Scattering. Quasi-elastic light scattering (QELS) experiments were performed to measure the apparent hydrodynamic diameter of the micelles. The scattered light of a polarized HeNe laser (632.8 nm) was measured at 90° and collected on a Brookhaven BI 9000AT correlator at 25.0 °C. The hydrodynamic diameter was calculated from the measured diffusion constant using Stokes equation. The polydispersity of the micelle is given by μ_2/Γ, where μ_2 is the second cumulant of the decay function and Γ is the decay rate of the scattering correlation function. The size distribution could also be obtained using the NNLS (v. 4.0) software supplied by Brookhaven.

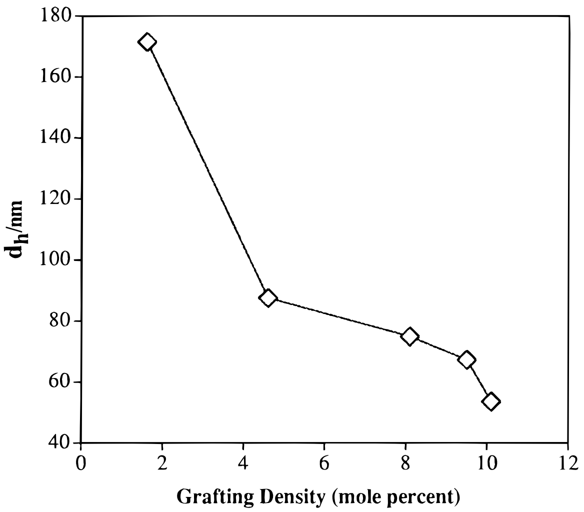

Figure 1. The hydrodynamic diameter (d_h) as a function of the grafting density. These micelles were prepared by injection 0.5 mL of a 2 mg/mL solution of polymer in dioxane into 5 mL of 1 mM NaCl aqueous solution.

Static Light Scattering. The apparent weight-average molecular weight of micelles were measured on a modified FICA 50 photometer equipped with a mercury lamp. All experimental light scattering data were analyzed by the Zimm method. Five concentrations (typically from 0.1 to 0.01 mg/mL) of each micelle sample were measured as a function of scattering angle. Zimm plots were extrapolated to zero concentration and scattering angle to obtain the molecular weight of the micelle. The refractive index increment value, d*n*/d*c*, was estimated to be 0.226 mL/g based on the copolymer composition and standard values of PAA and PS latexes in water.[15]

Transmission Electron Microscopy. Transmission electron microscopy (TEM) was used to observe the morphology of the micelles. A JEOL TEM 200 CX transmission microscope was used at an accelerating voltage of 120 kV. Samples were prepared by freeze-drying dilute solutions of micelles in water on a thin carbon film layered over a copper grid.

Fluorescence Spectroscopy. Steady-state fluorescence spectra were taken on a Spex Fluorolog fluorometer with double monochromators for both the excitation and emission radiation. The data were collected and stored using DM3000 software from Spex.

Results and Discussion

(a) Dependence of Size of Micelle on Grafting Density of Polystyrene. The dependence of the hydrodynamic diameter of the micelles on the grafting density of styrene is shown in Figure 1. For this data set all micelles were prepared by injecting 0.5 mL of a solution of 2 mg/mL of polymer in dioxane into 5 mL of 1 mM aqueous NaCl. These results suggest that the higher the grafting density of the hydrophobic polystyrene grafts the smaller the diameter of the micelles, although there is very little difference in G3−G5. We choose to emphasize copolymer G5 in the results reported herein. The micelles from copolymer G1 were quite large and not very stable. Because of the small number of PS grafts, this polymer is more like a telechelic associating polymer.[16]

When graft copolymers form micelles in solvents that are thermodynamically good for the grafts, it has been found that the higher the number of grafts the lower the micelle aggregation numbers.[17] This relationship can be rationalized as arising from the requirement that there is a constant area per emerging chain of the corona from the core.[17,18] For the present polymer system, the dependence of the hydrodynamic diameter on grafting density is relatively weak, with all polymers similar to each other except for sample G1 with the lowest grafting density. In general, the hydrodynamic diameter is not a direct measure of aggregation number, especially in the present case because the morphology of these micelles appears to be very different from classical spherical micelles (see TEM images discussed below).

Price et al. studied the thermodynamics of micelle formation of block copolymers using various techniques such as light scattering, electron microscopy, and calorimetry.[19] It was concluded that the enthalpic contribution to the free energy change is responsible for the association of block copolymers in organic solvents or solvent mixtures. We believe that the aggregation of PAA-*graft*-PS in aqueous media is also an enthalpy-driven process. The main contribution to the negative enthalpy change comes from strong interactions between the insoluble polystyrene blocks. Balsara et al. have discussed micelles made from BAB triblock copolymers in solvents that are good for the A block and have pointed out that the entropic penalty resulting from the loops in the corona was not particularly severe.[20] It has been reported that telechelic polymers have the potential to form gels at some polymer concentration due to the bridging of the micelles to produce “flowers”.[21] Kikuchi and Nose have recently studied micelles formed by PMMA-*g*-PS in a selective solvent for PMMA. It is not clear if the rate of nonsolvent addition plays any role in their observations, but they do observe a concentration dependence in the micelle formation upon cooling that is analogous to our observations. We will come back to this work in the Summary. Most theories of micelle formation are based on equilibrium thermodynamic considerations. Our micelles are most decidedly not prepared under equilibrium conditions and should be regarded as kinetically controlled species. Nevertheless we find the reproducibility and stability to be excellent (it is likely that the stability is aided by the glassy polystyrene portion of the structure).

If the concentration of PAA-*g*-PS added to water is sufficiently high it is reasonable that the PS grafts of different copolymers associate in the formation of a polystyrene aggregate. This is borne out by the aggregation numbers discussed later. In Figure 2 we present the TEM image of micelles prepared from copolymer G5 (made by adding 4.4 mg/mL of dioxane solution to 5 mL 1 mM NaCl solution). These images demonstrate that the micelles formed under this condition consist of multiple polystyrene cores surrounded by PAA loops. The size of these multicentered aggregates agree almost perfectly with the hydrodynamic diameter of 100.5 nm measured by QELS (Table 2). It seems likely that the morphology of the micelles formed under our conditions will vary in a complex way on the polymer concentration and/or solvent conditions (e.g. pH, ionic strength). This is certainly true of the gross features of the particle (molecular weight, R_g, d_h) as is discussed in the next subsection.

(b) Effect of Copolymer Solution Concentration on Micelle Properties. Figure 3 illustrates the increase of the diameter of micelles for the G5 copolymer with the concentration of copolymer in the dioxane that is added directly to 1 mM NaCl aqueous solution.

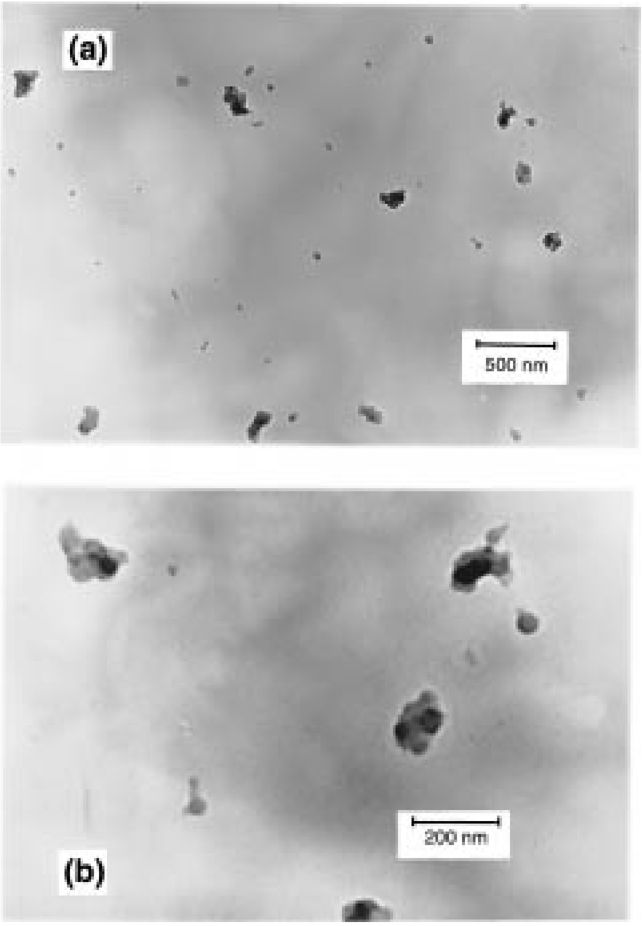

Figure 2. TEM image of the micelles prepared from copolymer G5. The concentration of the polymer used to prepare this sample was 4.4 mg/mL in dioxane and the hydrodynamic diameter was 100.5 nm (see Table 2). For (a) and (b) the magnification was 20K and 60K, respectively.

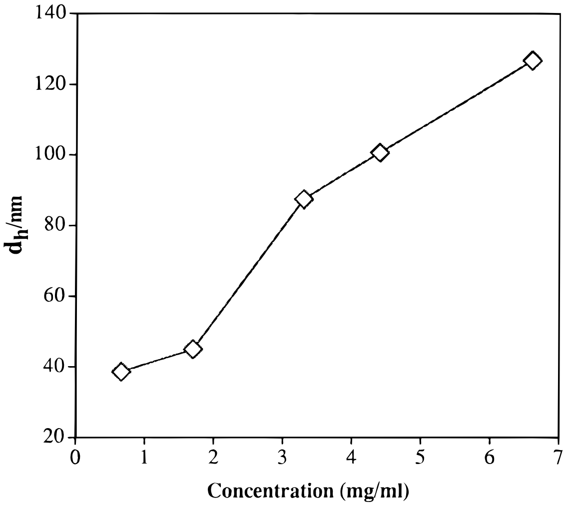

Figure 3. The hydrodynamic diameter (d_h) as a function of the concentration of G5 in dioxane added to 1 mM NaCl water.

Micellization from dioxane solutions more concentrated than indicated in Figure 3 results in white milky solutions that consist of large aggregates. This dependency further demonstrates the kinetically controlled nature of these micelles. The well-behaved aqueous micelle solutions represented in Figure 3 can be concentrated by a factor of 20 after preparation (see later discussion).

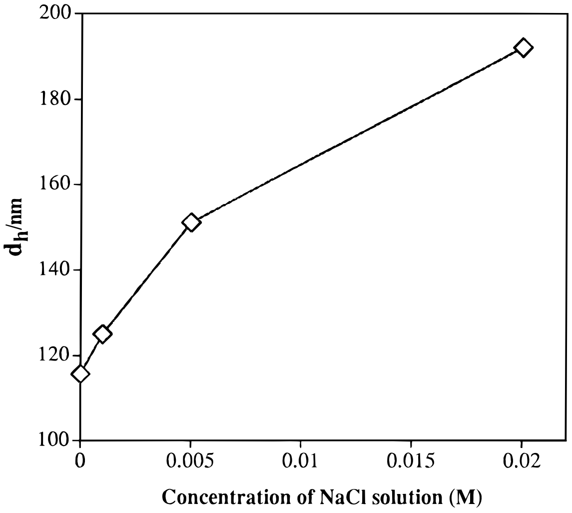

Figure 4. The hydrodynamic diameter (d_h) as a function of the ionic strength of the aqueous phase (concentration of G5 in dioxane is 6.6 mg/mL).

Static light scattering with Zimm plot analysis was carried out to measure the molecular weight of the micelles prepared at different stock solution concentrations. Table 2 presents the molecular weight data for G5 micelles and the estimated aggregation number for four different stock solution concentrations.

Burchard has discussed the sensitivity of the ratio R_g/R_h ($=\rho$) to the shape and polydispersity of polymers in solution.[22] In particular, for a homogeneous sphere ρ is 0.775, for monodisperse rodlike polymers ρ can exceed 5 (polydispersity pushes this ratio higher), and for regular star polymers ρ is in the range 1.5 to ca. 1.1. For polymer micelles composed of diblock polymers we have found ρ to approximate the homogeneous sphere value.[5e,23] Kikuchi and Nose found the variation of ρ with molecular weight of associating polymer micelles to be a useful diagnostic, varying from ca. 1 for unimolecular micelles to ca. 2.3 for associated multi-polymer micelles.[9] We also observe a variation of ρ with aggregation number. For the samples prepared at the three highest concentrations ρ varies smoothly from 0.772 to 2.10 (Table 2). However, the sample prepared with 1.7 mg/mL has a ρ value consistent with a more highly branched structure.[24] As stated above, we suspect that gross features of these particles are not only a function of the preparation conditions but also of the morphology of the final particles. Studies of PAA-*g*-PS using monodisperse PAA and variable molecular weights of PAA and PS will address these issues in more detail.[25]

(c) Effect of Ionic Strength of Aqueous Solution. In Figure 4 the diameter of the micelles made from G5 (6.6 mg/mL in the stock dioxane solution) is plotted against the concentration of the NaCl in the aqueous phase (neutral pH). It is reasonable that at higher ionic strength electrostatic screening of the PAA polymers is more efficient, reducing the energetic barrier to association of the hydrophobic PS chains.

(d) Effect of pH on Hydrodynamic Diameter. For this study the micelle sample was made by adding 0.5 mL of a 5.0 mg/mL G5 dioxane solution to pure water. Then NaCl was added to change the ionic strength to the final values. Micelle solutions at various ionic strengths were then titrated with NaOH solution and the hydrodynamic diameter was monitored by

Table 3. pH and Ionic Strength Effects on the Hydrodynamic Diameter of G5 Micelles[a]

no NaCl		1 mM NaCl		5 mM NaCl		20 mM NaCl	
pH[b]	d_h	pH	d_h	pH	d_h	pH	d_h
6.18	81.8 ± 0.5	6.02	77.6 ± 0.8	5.52	75.5 ± 1.1	5.26	74.8 ± 1.4
7.07	79.0 ± 1.8	6.95	76.2 ± 1.0	6.60	74.2 ± 1.8	6.20	74.2 ± 1.2
7.70	78.9 ± 0.8	7.47	75.8 ± 1.7	7.17	74.1 ± 0.7	6.75	74.3 ± 0.1
8.39	76.6 ± 0.4	8.15	75.5 ± 0.8	8.24	73.1 ± 1.4	7.97	73.9 ± 1.1
10.51	79.5 ± 1.0	10.35	73.5 ± 0.6	10.44	77.0 ± 0.9	10.32	76.9 ± 0.7
		11.78	76.7 ± 1.3	11.78	76.9 ± 1.6	11.68	76.7 ± 0.9

[a] Micelles prepared by adding 0.5 mL of 5 mg/mL of G5 polymer to 5 mL of pure water and dialyzing against pure water. NaCl was then added to obtain the final ionic strength. [b] Small amounts of NaOH solution added to vary pH.

QELS. The hydrodynamic diameters as a function of pH for various ionic strengths are tabulated in Table 3. There is virtually no change of d_h with pH, unlike diblock polymers.[26] These data also illustrate that the d_h values do not reflect long-range interactions between the charged micelles which would be very sensitive to ionic strength.

We believe that this reflects the fact that relatively few free dangling PAA chains extend into the solution from micelles and most of the PAA chains are involved in forming loops that are anchored to the surface of insoluble polystyrene cores. Since the PAA chains are anchored to the multiple cores of the micelles, the normal chain expansion of deprotonated PAA is prevented. This is consistent with the morphology revealed in the TEM images discussed earlier, although we do not know if this morphology is found under all the various preparation conditions described herein. We also note that for polymer G5 there are only an average of 9 carboxylate groups between PS grafts (Table 1).

(e) Stability of the Micelles. Four weeks after a micelle solution was prepared by adding 6.6 mg/mL of G5 dioxane solution to 5 mL 1 mM NaCl aqueous solution, the size and polydispersity of the micelle were measured again with QELS. No appreciable change in size or polydispersity was observed. To find out if the micelles would be modified when the sample was concentrated, 100 mL of the micelle solution was prepared in the same manner. Then the solution was condensed by evaporating the water using a rotary evaporator at 25 ± 2 °C. When the final volume of the solution was reduced to around 5 mL, a white milky solution started to appear and the evaporation was stopped. Two drops of the condensed solution were taken and diluted to 2.0 mL with 1 mM NaCl solution and characterized by QELS. The size and polydispersity matched those of micelles before condensation.

(f) Solubilization of Pyrene. Pyrene was solubilized into the micelle as follows: 1.0 mg pyrene was added to 0.5 mL of a 4.4 mg/mL G5 solution in dioxane. The solution was added dropwise to 5 mL 1 mM NaCl solution under stirring. The micelle solution was dialyzed against water saturated with pyrene. Afterward, the solution was filtered through a 0.45 μm PTFE filter, which is known from separate experiments to remove microcrystals of pyrene. This solution was used for the TEM sample preparation and fluorescence measurement. The TEM images of the resultant micelles reveal simple spherical shape with a diameter that approximates the hydrodynamic diameter (image not shown). We presume that the gross change of morphology is the result of the stabilization of small particles of pyrene by the PAA-*g*-PS polymer. The fluorescence spectrum contains a substantial contribution from the excimer (see Figure 5). Solubilization and release studies of these micelles are ongoing and will be reported separately. It is worth noting that the solubilization of ca. 0.2 mg/mL of pyrene in water is approximately 2400 times more concentrated than the intrinsic solubility of pyrene in water,[27] despite the relatively low concentration of the micelle. Compared to micelles prepared from polystyrene-*block*-poly(methacrylic acid) loaded by an equilibrium method,[28] this solubilization procedure is ca. 21 times more effective per gram of polymer (e.g. compare 0.105 and 2.25 mmol of pyrene/mg of polymer).

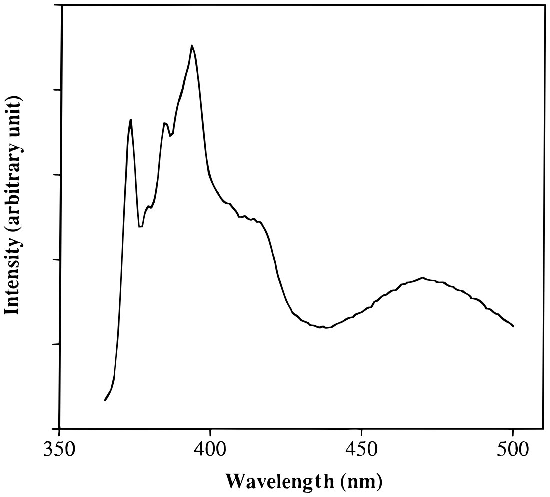

Figure 5. Fluorescence spectrum of pyrene solubilized by G5 micelle.

Summary

We have described the preparation and characterization of micelles based on poly(acrylic acid)-*graft*-polystyrene polymers. While there is some dependence of micelle properties on the grafting density, it is much weaker than found for the case that the graft polymer forms the corona.[17] In this paper we have concentrated on characterizing the dependence of the micelle properties on the conditions of preparation. In our approach we inject a dioxane solution of the polymer into water containing NaCl. The hydrodynamic diameter and molecular weight of the micelle depend on the concentration of the polymer in the dioxane solution and the ionic strength of the aqueous phase. It is perhaps surprising, given the harsh conditions of preparation, that these micelles have a well-defined size distribution according to QELS.[29] Because of these dependencies, one can exercise considerable control over the size of the final micelle for the same polymer system. This seems to us to be a unique advantage of these materials. While the concentration of the micelles must be kept below an upper limit during preparation, the final micelles are quite stable and can be concentrated by a factor of at least 20 without aggregate formation.

The TEM images of a typical preparation reveal a unique micelle morphology in which small spherical cores (presumably polystyrene) are joined together in a "multicore" structure. This is consistent with the very small pH dependence of hydrodynamic diameter for already prepared micelles, in sharp contrast to diblock polymers with a core–polyacid corona.[26] Future studies will determine if this morphology is general or is also a function of the preparation conditions.

These polymers also can be used solubilize pyrene very efficiently and simply, and the resultant particle has a simple spherical morphology. We presume that this is the result of pyrene microcrystals (ca. 50 nm) acting as nucleation centers for the collapsing PS chains. Solubilization studies will be reported separately.

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