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Micellization of Ionic Block Copolymers

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1. Introduction

The investigation of ion-containing block copolymers in solution has revealed that these materials form spherical aggregates, known as micelles, in both water and organic solvents.[1−4] Studies of the formation and characteristics of these aggregates have generated a great deal of interest, as micelles of ionic block copolymers provide an extremely versatile addition to the growing field of molecular self-assembly. Possible applications in the areas of advanced materials and drug delivery have spurred our own interest in this field.

For many years, the phenomenon of micellization has been known to occur in solutions of low molecular weight amphiphiles (or surfactants) above a concentration known as the critical micelle concentration (cmc). The cmc is a function of both the amphiphile and the solvent environment and also tends to vary with the method of detection. However, in general terms, we can state that only single amphiphiles exist in solution below the cmc while, above the cmc, associates (or aggregates) tend to form. Based on the kinetics of exchange between the unimers and their self-assembled structures, the term "associate" is generally reserved for surfactant micelles, while micelles of block copolymers are often referred to as "aggregates". This point will be further discussed later on.

To understand the formation of spherical micelles, it is important to realize that amphiphilic molecules consist of both an ionic or nonionic polar moiety and at least one hydrocarbon chain. Since these two parts of the molecule have very different solubilities, amphiphiles in solution above the cmc will tend to undergo microphase separation. For example, in an aqueous environment, the hydrocarbon chains of a number of aerosol OT (AOT) molecules will cluster together to form a liquid-like core, surrounded and protected by the solubilized ionic head groups.

The subject of the present Account is the self-assembly of ionic block copolymers, which is in many ways analogous to the micellization of surfactants in solution. In our discussion, we hope to show that the combination of extremely high aggregate stability, low cmc's, and a wide range of aggregate sizes gives ionic block copolymers unprecedented versatility and opens the door to many potential applications. Before embarking on a description of ion-containing block copolymers, however, a more general discussion of block copolymer micellization is required.

It has long been known that block copolymers in selective solvents will form spherical aggregates, with compact cores of insoluble blocks surrounded by a soluble corona composed of soluble blocks. Like their surfactant counterparts, micelles of block copolymers show an extremely narrow size distribution. The term micelle has been applied to these colloidal aggregates, due to the structural similarities with surfactant micelles; however, we shall see that micelles of block copolymers and low molecular weight surfactants are quite different in terms of their lability and exchange kinetics. For a number of years, block copolymer micelles have been the subject of much interest, and some excellent reviews have been published in the field.[5−7]

Along with a number of experimental studies, block copolymer micelles have been the subject of considerable theoretical treatment in recent years.[8−21] Of particular relevance to the present review are theories proposed by Zhulina and Birshtein[12] and by Halperin[16] for "star" micelles. These micelles are spherical with small cores and expanded coronas, and form when the length of soluble block is considerably longer than that of the insoluble block. Conversely, "crew-cut" micelles[22,23] are structures with large cores and short

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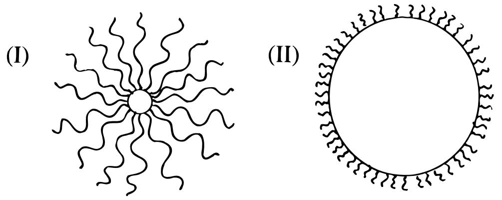
Chart 1. Schematic illustration of (I) a star and (II) a crew-cut micelle.



coronal "hair", formed from asymmetric block copolymers with relatively long insoluble blocks (Chart 1). In the former case, theory predicts that the radius of the core (R_c) is independent of the soluble block length and scales as $N_B^{3/5}$, where N_B is the number of units in the insoluble block.

At this point, it is important to mention that the theoretical treatment of block copolymer micelles, resulting in scaling relations such as the one given above, is generally based on thermodynamic considerations and assumes an equilibrium between single chains and the micellar aggregates. Unlike associates of surfactants, which are extremely labile structures, the kinetics of exchange between block copolymer micelles and single chains in solution are slow, due to the high viscosity of the insoluble blocks within the micelle core. This is especially true in the case of the ionic block copolymer micelles which pertain to the present discussion; these have glassy polystyrene cores in an aqueous environment, or ionic cores with short-range electrostatic interactions in organic environments. In fact, on a reasonable time scale, the micelles of ionic block copolymers may be regarded as "frozen" structures, with no dynamic equilibrium between micelles and single chains. An application of theoretical models to such systems, therefore, requires us to assume that a dynamic equilibrium does exist at some stage of micelle formation, even though the final result is a frozen aggregate. These considerations should be kept in mind throughout the present review, as they serve to qualify our use of the term "micelle" in describing frozen aggregates of block copolymers.

Several theoretical treatments of block copolymers in selective solvents have addressed the phenomenon of the critical micelle concentration.[9,18−20] However, until very recently, the polydispersity of the insoluble blocks had not been properly considered. In a new model for the micellization of block copolymers in solution, Gao and Eisenberg[21] refined the treatment of Holland and Rubingh,[24,25] in order to account for the polydispersity effect of the insoluble blocks on the cmc. The model describes the collapse of insoluble blocks into colloidal spheres below the cmc, such that the driving force for micellization is the van der Waals interaction between spherical particles.

To illustrate the effect of polydispersity on the cmc, a plot of single-chain concentration (S) as a function of total block copolymer concentration for a polystyrene-b-polyisoprene (PS-b-PI)/n-hexadecane system is shown in Figure 1.[21] For an average insoluble block length of 67 styrene units, the concentration of single chains is plotted for various polydispersity indexes (P.I.). The horizontal line above the cmc for P.I. = 1.00 indicates a sharp pseudo-phase-transition, which, for polydisperse systems, is replaced by a continued increase in S with concentration above the cmc. As a result, the cmc (denoted by arrows in the figure) decreases with increasing P.I. and becomes much less distinct.

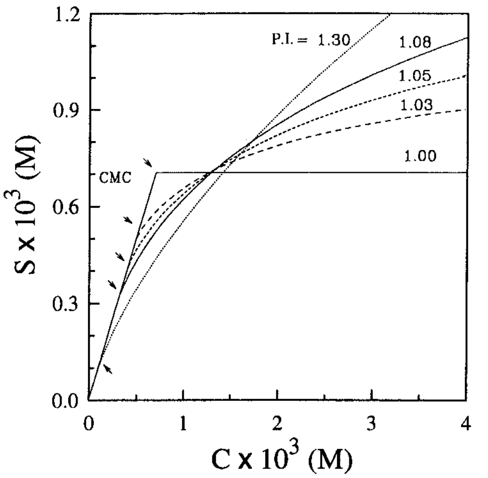


Figure 1. Single-chain concentration as a function of the total block copolymer concentration at different polydispersity indexes in the PS-b-PI/n-hexadecane system for a polystyrene block length of 67 units.

We now turn our attention to the colloidal behavior of ionic block copolymers, which possess both hydrophilic blocks of ionic repeat units and hydrophobic blocks of nonionic units. In an AB diblock, for example, a block of nonionic A units is covalently linked to a block of ionic B units. Due to the high degree of incompatibilty between the ionic and nonionic blocks, ionic block copolymers in solution exhibit extremely low cmc's[26−28] and high aggregate stability.[3,4]

Ionic block copolymers in solution can be divided into two main categories: block polyelectrolytes and block ionomers. From the definitions of polyelectrolytes and ionomers proposed by Eisenberg and Rinaudo,[29] it follows that the properties of block polyelectrolytes are governed by electrostatic interactions over the relatively large distances within the corona and between the micelles, while the properties of block ionomers are governed by short-range interactions within the micelle core.

The classification of ionic block copolymers as either block polyelectrolytes or block ionomers is determined by the nature of the solvent. Ionic block copolymers in water are block polyelectrolytes, forming micelles with nonionic cores and coronas made up of the soluble ionic blocks. In organic solvents, ionic block copolymers can be described as block ionomers, with ionic micelle cores surrounded by the nonionic soluble blocks. Following the terminology adopted for surfactants, ionic block copolymers in aqueous and nonaqueous solvents are sometimes referred to as regular and reverse micelles, respectively. In the "star micelle" regime, block ionomers generally have long nonionic blocks and short ionic blocks, whereas block polyelectrolytes have long ionic blocks and short

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nonionic blocks. The so-called "crew-cut" polyelectrolytes, on the other hand, have relatively short ionic blocks, surrounding a large nonionic core. "Crew-cut" micelles of block ionomers, to our knowledge, have not been investigated.

This paper will present an overview of the literature on ionic block copolymers in nonaqueous and aqueous solutions, with particular emphasis on work performed in this group. We will begin with a summary of the recent work on block ionomer micelles, followed by a discussion of block polyelectrolytes.

2. Ionic Block Copolymers in Organic Solvents (Reverse Micelles)

The ionic block copolymers which have been most extensively studied in organic solvents are the polystyrene-based diblock ionomers with long polystyrene blocks joined to relatively short ionic blocks. Diblock ionomers of this type, in which the ionic block is poly(metal acrylate), poly(metal methacrylate), or quaternized poly(4-vinylpyridine), will be the focus of the present discussion. However, it is worth mentioning that an investigation of quaternized polystyrene-*b*-poly(4-vinylpyridine)-*b*-polystyrene (PS-*b*-P4VP-*b*-PS) triblock ionomers in THF has also been reported.[30] Another related system is sodium-neutralized poly(*tert*-butylstyrene)-*b*-lightly sulfonated polystyrene, which has recently been studied by light scattering in nonpolar solvents.[31]

The following section on reverse micelles of ionic block copolymers will be divided into four parts. The first part will deal with the characterization of fundamental parameters of block ionomers using numerous techniques (size-exclusion chromatography, light scattering, small-angle X-ray scattering, etc.). The second part will discuss the problem of cmc determination of block ionomers. Next, nuclear magnetic resonance (NMR) investigations of the solubilization of water into the ionic cores and the dynamics of the soluble corona will be described. Lastly, an interesting application of block ionomers will be presented: the size control of quantum-confined nanoparticles within a polymer host.

2.1. Characterization of Fundamental Parameters. Until quite recently, experimental work on the properties of ionic block copolymers in organic solvents was very limited. In the first detailed study of diblock ionomer reverse micelles,[3] the aggregation behavior of polystyrene-*b*-poly(sodium methacrylate) (PS-*b*-PMANa) and polystyrene-*b*-poly(cesium methacrylate) (PS-*b*-PMACs) copolymers was investigated in solvents selectively good for the polystyrene block (e.g., dimethylformamide (DMF), tetrahydrofuran (THF)). Using size-exclusion chromatography (SEC) coupled with intrinsic viscosity measurements, micellar characteristics such as aggregation number and hydrodynamic radius were investigated systematically as a function of the ionic and polystyrene block lengths.

Typical size-exclusion chromatograms of block ionomers in selective solvents show up to three distinct peaks, attributable to micelles, single chains, and homopolystyrene.[3,32] The micelle peak appears at the lowest elution volume, due to the large size of the micellar aggregates relative to that of the unimers. The relative area under the micelle and single-chain peaks depends on the composition of the block ionomer, with longer ionic blocks resulting in a higher percentage of micellized material.

When a mixture of micelles with different molecular weights was injected repeatedly into the SEC column, the bimodal shape of the chromatogram was retained over 3 days, indicating the lack of a dynamic equilibrium between micelles and single-chains.[3] The existence of a single-chain peak was attributed to a distribution in the length of the ionic block, with single chains having a lower ion content than aggregated chains. Infrared spectroscopy of micelle and single chain fractions supported this hypothesis. Despite the absence of a dynamic equilibrium, the term micelle is used for block ionomers, on the basis of the structural and behavioral similarities with other block copolymer micelles.

A combination of SEC and viscometry was used to determine aggregation numbers and hydrodynamic radii (R_h) of polystyrene-*b*-poly(metal methacrylate) reverse micelles.[4] Both the aggregation number and the hydrodynamic radius were found to increase as the length of the insoluble block increases. However, as the length of the soluble block increases, the aggregation number decreases and the hydrodynamic radius increases. The latter trend is understood on the basis of an increase in the corona thickness as the length of the polystyrene segment increases; thus the overall radius of the micelle increases, despite a lowering of the aggregation number.

The above trends were confirmed by dynamic light scattering (DLS) measurements.[4] DLS was also used to test the stability of reverse micelles by the addition of polar solvents to different solutions of block ionomers. After an initial decrease in R_h upon addition of the polar solvent, the sizes of reverse micelles were found to remain constant over a period of several months.

One of the attractive features of block ionomer micelles is the wide range of aggregate sizes which are possible in these systems, as micellization is found to occur down to very short ionic block lengths. In fact, when the length of the ionic block is reduced to a single ionic unit, one obtains a useful conceptual bridge between micelles of block copolymers and those of surfactant amphiphiles, which generally possess a single ionic head group. Related to this discussion are the telechelic ionomers,[33] in which single ionic groups or zwitterions are fixed to both ends of the polymer chain, and the monochelic ionomers,[34−37] in which an ionic moiety is fixed to one end of the chain. In the case of monochelics, viscometry and static light scattering (SLS) have been used to determine cmc's and aggregation numbers of carboxylate-terminated polystyrene chains in solvents of low dielectric constant.[36]

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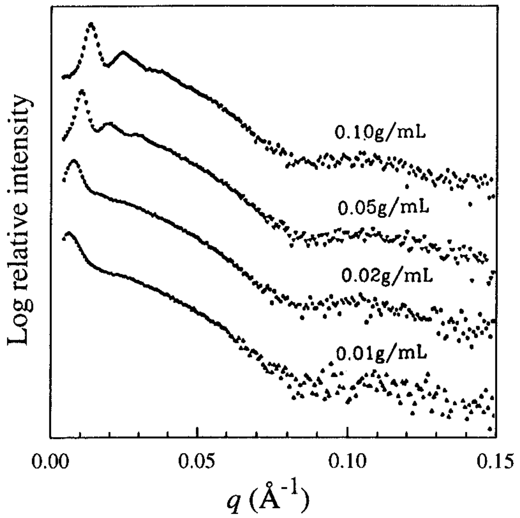

Figure 2. SAXS profiles of PS(600)-*b*-PACs(45) diblock ionomer in toluene in the concentration range 0.01–0.10 g/mL.

The aggregation behavior of 1,2-dicarboxyethyl-terminated polystyrene in cyclohexane has also been studied.[37]

It has been found that small-angle X-ray scattering (SAXS) is a useful technique for obtaining structural information on block ionomer micelles. SAXS has been used to investigate micellar core sizes of polystyrene-*b*-poly(cesuim acrylate) (PS-*b*-PACs) and PS-*b*-PMACs in toluene for several ionic block lengths.[38] Typical SAXS profiles for block ionomer micelles (Figure 2) are a combination of a shape factor, which characterizes the size and shape of the scatterers (i.e., the ionic cores), and the structure factor, which characterizes distances between scatterers. The structure factor can also be related to order within the micelle solution.

From such scattering profiles, core sizes of the PS-*b*-PACs and PS-*b*-PMACs systems were found to obey the star model, scaling as $N_B^{3/5}$, independent of the PS block length. A proportionality constant of 6.5 Å was determined. The applicability of a thermodynamically-derived scaling relation is a good indication that block ionomer micelles, although undoubtedly frozen structures, approach equilibrium in the early stages of micelle formation. These micelles are formed by neutralization of single chains of acid-form block copolymers in organic solvent; before the core-forming blocks are 100% neutralized,[39] it is likely that micelles and single chains are in dynamic equilibrium. At some point, the equilibrium structures become frozen as solvent is excluded from an increasingly ionic core.

In further SAXS work,[40] the study of block length dependence was extended to include quaternized PS-*b*-P4VP. The same fit with the Halperin model was obtained, supporting the relationship $R_c = 6.5N_B^{3/5}$ Å. High chain extension in the micelle core was observed for both ionic microdomains dispersed in a nonionic matrix and nonionic microdomains dispersed in an ionic matrix.[41] This result proved that chain extension within the cores of block ionomers is due to the minimization of interfacial energy rather than to short-range ionic interactions. SAXS results, together with computer modeling of spherical shape factors, have been used to determine the radii polydispersity indexes (RPI) of ionic cores.[38] These were found to be between 1.02 and 1.04, considerably smaller than the polydispersity indexes of the polymer chains.

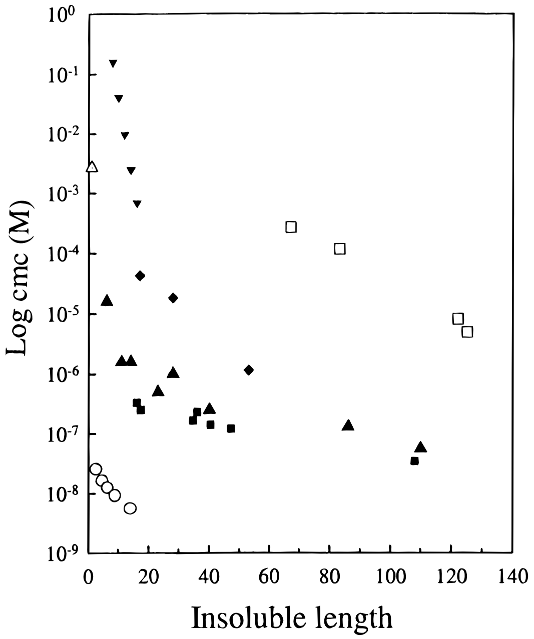

Figure 3. cmc values for different micellar systems: AOT (△),[44] sodium alkyl sulfonate surfactants (▼),[44] PS-*b*-PI (□),[43] poly(ethylene oxide)-*b*-poly(butylene oxide)-*b*-poly(ethylene oxide) (PEO-*b*-PBO-*b*-PEO) (◆),[46] PS-*b*-PANa (▲),[26] PS-*b*-PEO and PEO-*b*-PS-*b*-PEO (■),[45] and PS-*b*-PANa (○).[27] The filled and hollow symbols represent aqueous and organic media, respectively.

2.2. Critical Micelle Concentrations of Block Ionomers. A wide range of techniques have been used to determine the critical micelle concentrations of block copolymers in selective solvents, such as fluorescence, osmometry, viscometry, and static light scattering. The latter method is sensitive to changes in the apparent weight-average molecular weight (M_w) of the solution, a quantity which includes contributions from both micelles and single chains. In a typical experiment, the quantity $Kc/R(0)$ (where K is the optical constant and $R(0)$ is the Rayleigh ratio extrapolated to 0 angle) is plotted as a function of concentration; since $Kc/R(0)$ is inversely proportional to the apparent M_w, such a plot shows three distinct regions, corresponding to unimers in solution, a transition region, and micelles in solution.

The extremely low cmc's of block ionomer micelles make their determination by empirical methods difficult, as the unimer region is often at concentrations below the limit of detection. However, the cmc's can be evaluated by fitting the micelle and transition regions according to an equation proposed by Debye.[42] For systems with significant polydispersity in the insoluble block, a new method has been developed,[26] based on the micellization model of Gao and Eisenberg.[21] Figure 3 shows plots of cmc vs the insoluble block length for various systems,[43–46] including AOT surfactant in benzene and nonionic block copolymers

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in selective solvents. From these plots, one can compare the extremely low cmc's of block ionomer micelles with the wide range of cmc's observed for other self-assembling species.

2.3. Characterization of Water Solubilization and Chain Dynamics by NMR. An important feature of surfactant reverse micelles is their ability to solubilize water within the ionic core, creating water pools which can act as "microreactors" for hydrophilic reactants. Block ionomer micelles in nonpolar solvents are also able to solubilize small quantities of water, and the distribution coefficient of water between the ionic core and the solvent has been studied by proton NMR.[47,48] A single chemical shift for the water protons is observed, which is a weighted average of the chemical shift of water in the reverse micelle and in the nonpolar solvent. The appearance of a single chemical shift indicates that the exchange of water between the ionic core and the solvent phase is very fast within the time scale of the NMR experiment. On these grounds, it seems that the ionic core is liquid-like in the presence of water.

From measurements of the observed chemical shift of the water protons,[47] the distribution coefficients in favor of water solubilization in different solvents were found to occur in the following order: cyclohexane > benzene ≈ toluene > chloroform ≫ THF ≈ DMF. Distribution coefficients were also investigated for ionic blocks with different functional groups,[48] and at 25 °C they were found to decrease as follows: cesium carboxylate > sodium sulfonate ≈ sodium carboxylate >> pyridinium methyl iodide.

NMR has also proven useful in the measurement of coronal chain dynamics at the segmental level. In systems of PS-*b*-PACs in carbon tetrachloride (CCl_4), the mobility of ^{2}H-labeled polystyrene segments was probed at various distances from the ionic core.[49] ^{2}H relaxation times revealed that close to the ionic–nonionic junction there is a definite decrease in segmental mobility with respect to the "free" chain. Further from the ionic block, the segmental mobility is less restricted, and at a distance of ca. 40 units the mobility is close to that of the nonionic homopolymer. It was also found that segmental mobility decreased with increasing length of the ionic block. This result can be explained on the basis of geometrical considerations; for star-like micelles, the segmental density at a particular distance from the core is higher when the ionic core is larger, resulting in a larger number of steric interactions.

2.4. Semiconductor Nanoparticles in Block Ionomer Micelles. The control of ionic core sizes through variations in the insoluble block length make block ionomers attractive materials for the formation of polymer–nanoparticle composites. For example, the neutralization of polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) block copolymers can introduce a wide range of metal ions into the core; the reduction of these ions, or treatment with H_2S, will effect the formation of ultrasmall metal or metal sulfide particles within the cores,[50] with sizes determined by the aggregation number of the block ionomer host.[51]

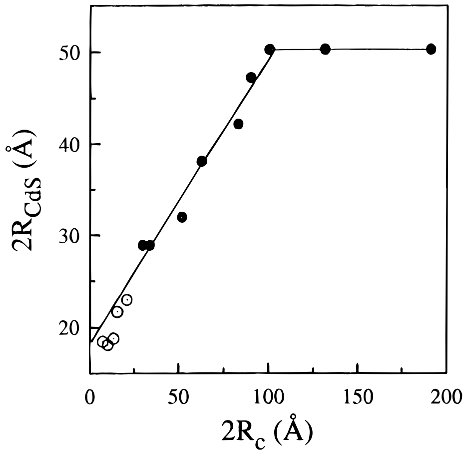

Figure 4. Plot of CdS particle diameter vs diameter of original core (calculated from $R_c = 6.5N_B^{3/5}$ Å). Dotted circles indicate CdS particles synthesized within the microdomains of random ionomers.

One such application of block ionomers has been demonstrated by the precipitation of quantum-confined CdS nanoparticles within the cores of polystyrene-*b*-poly(cadmium acrylate) (PS-*b*-PACd).[51] Quantum confinement arises from the extremely small sizes of these crystallites (<60 Å) and results in excited states which are more energetic than those of bulk CdS. To prepare the composites, the ionic cores were placticized with water, after which the films were treated with H_2S for 8 h. CdS particle sizes were determined from blue shifts in the UV–vis spectrum, and these were plotted against the size of the original core ($R_c = 6.5N_B^{3/5}$ Å). A linear relationship was found between CdS particle sizes and ionic core sizes, up to a particle diameter of 50 Å, where the particle sizes level off (Figure 4). Below 50 Å, it appears that excellent size control of CdS particles can be achieved by selecting the appropriate ionic core size. Also shown in the plot are CdS nanoparticles synthesized in the multiplets of random ionomers (dotted circles), which allow for synthesis of particles down to 18 Å.[52]

The stability of the CdS–polymer composites was shown by dissolving the materials in organic solvents (e.g., toluene, THF) to form clear yellow solutions of CdS-containing reverse micelles.[51] The micelles were stabilized by reneutralizing the PAA block with NaOH. The yellow powders were then repeatedly precipitated into MeOH and redissolved, without significant changes in the UV–vis absorption spectrum of the composite.

3. Ionic Block Copolymers in Aqueous Solutions (Block Polyelectrolyte Micelles). In this section, two types of block polyelectrolyte micelles will be discussed, star and crew-cut micelles. One of the earliest studies of block polyelectrolytes was performed by Schindler and Williams, in which phase separation in films of polystyrene-*b*-poly(vinylpyridinuim methyl bromide) was investigated.[53] Much of the pioneering

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work on block polyelectrolyte star micelles in solution was performed by Selb and Gallot, and their work has been reviewed.[1,2] It should be mentioned that the micellization of block polyelectrolytes on the surface of water has also been extensively studied.[54−58] However, in general, studies of block polyelectrolyte micelles have been scarce. To date there are two theoretical models dealing with the micellization of block polyelectrolytes.[19,59]

The following section will first focus on the characterization of aqueous star micelles by a variety of techniques. The effects of several factors, such as the solvent quality (i.e., salt concentration and temperature), block size, degree of neutralization, and solubilization, on micellization will be discussed. In the second part of this section, an overview of aqueous crew-cut micelles and a number of related morphologies will be addressed.

3.1. Characterization of Star Micelles. The solvent quality has been found to influence the micellization of block copolymers. In general, when the solvent quality decreases, the solubility of the chains decreases, resulting in a lowering of the cmc and an increase in the aggregation number of the micelles. The quality of the solvent for block polyelectrolyte chains can be influenced, for example, by adding salt or by changing the temperature. The effects of solvent quality on the micellization of two block polyelectrolyte systems, polystyrene-*b*-poly(4-vinyl-*N*-ethylpyridinium bromide) (PS-*b*-P4VPEtBr) and PS-*b*-PANa, as well as the influence of block lengths, will now be discussed.

The solvent quality for PS(26)-*b*-P4VPEtBr(140) in a water (34 wt %)/methanol mixture was explored as a function of LiBr concentration by SLS and sedimentation velocity.[1] It was found that the weight fraction of the micelles and the apparent M_w increased with the addition of LiBr at low salt content and remained essentially constant at and above 0.2 M LiBr concentration. At very low salt concentrations (0.01 M), no micelles were present. For some of the low salt concentrations, a cmc was observed which was found to decrease as the salt concentration increased. The effect of temperature on the cmc and the apparent M_w was studied for this sample at different salt concentrations. An increase in temperature resulted in an increase in the solvent quality and thus an increase in the cmc and a decrease in the aggregation number.

The effect of the solvent quality on micellization was found to depend on the length of the copolymer blocks. For instance, Selb and Gallot found that, for short PS block lengths (<ca. 30 units), the cmc and molecular weight were strongly affected by the salt concentration. However, for larger PS block lengths (>ca. 30 units), the effects of temperature and salt concentration were less significant. Thus, it can be suggested that, at high PS block lengths, the micellization process is dominated primarily by the insoluble PS blocks.

Block polyelectrolytes formed from PS-*b*-PANa in aqueous solutions have also received considerable attention.[26,28,60] In this system, micelle formation occurred when single chains of PS-*b*-PAA were dissolved in methanol, due to microphase precipitation of the polystyrene blocks. The micelles were then neutralized by the addition of NaOH, and the subsequent ionic form precipitated from solution. It has been observed that block copolymer micelles consisting of hydrophobic−hydrophilic segments are difficult to dissolve directly in aqueous solvents.[2] However, in the case of PS-*b*-PANa, heating the aqueous solutions at 100 °C for a period of time rendered the copolymer micelles soluble. This heating process was followed by viscometry and SLS.[26,60] Due to their glassy cores, these aqueous micelles are most likely kinetically frozen aggregates at normal concentrations, although we shall see that they do exhibit a cmc at very high degrees of dilution.

The cmc's of PS-*b*-PANa in water are shown in Figure 3.[26] These values were determined by fluorescence measurements using previously established methods.[45] It was found that the PS block length has a much greater effect on the cmc than the soluble PANa block length. For instance, an increase in the PS block length from 6 to 110 units, for a constant PANa block length of 1000 units, decreased the cmc by a factor of 320, while an increase in the PANa block length from 300 to 1400 lowered the cmc by a less than a factor of 2.[26]

A recent study explored more systematically the effects of the PANa block length and salt concentration on the cmc values.[28] A wide range of samples were investigated, with PS block lengths ranging from 6 to 110 units and PANa block lengths ranging from 44 to ca. 2400 units. For two series consisting of PS blocks of 11 and 23 units, it was observed that the cmc increased as a function of the PANa block length, passed through a maximum, then decreased as the PANa block length increased further. This maximum can be explained by a balance of solubility effects. The change in the cmc values with increasing PANa block length was found to become less dramatic for longer PS block lengths (e.g., 110 units), in agreement with results of Selb and Gallot.

The effect of NaCl concentrations (C_s) (0.1−2.5 M) on the cmc was also investigated for the PS-*b*-PANa system.[28] The cmc values were found to decrease when the salt concentration increased, and log cmc versus $C_s^{1/2}$ was linear for most of the series investigated. The slope, $d(\log \text{cmc})/d(C_s^{1/2})$, was found to be a function of the PS block length. For three different series with PS block lengths of 6, 11, and 23 units, $d(\log \text{cmc})/d(C_s^{1/2})$ plotted against the PANa length exhibited sigmodal behavior. This relationship was related to conformational changes of the polyelectrolyte chain as a function of the PANa block length.

SLS has been used to characterize aggregates of PS-*b*-PANa in 2.5 M NaCl.[60] It was found that for short PS block lengths (i.e., 6 units) the aggregation numbers were strongly affected by the PANa block length. However, as the PS block length increased, the effect of the PANa block length on the aggregation numbers decreased. Aggregation numbers, calculated core

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radii, and radii of gyration (R_g) were compared with the scaling predictions of the star model. It was found that the scaling relations were a good representation of the R_c and R_g values. The calculated R_c values for this system in 2.5 M NaCl agreed with the values determined by SAXS for similar samples measured in the solid state.[41] This result implies that, for the present system, the morphology of these micelles is the same in the solid state and in solution.

Micelles of polystyrene-*b*-poly(methacrylic acid) (PS-*b*-PMAA) have been extensively studied in mixed solvents of dioxane/water and water.[61−66] It has been pointed out that such micelles may be kinetically frozen when the solvent is very poor for the PS core (i.e., water rich solvents). The micellization process and coronal structure are influenced by the degree of neutralization (α) of the polyelectrolyte, as observed by Kiserow et al.[63] using DLS, viscosity, and SLS. At low concentrations and ionic strengths, the apparent hydrodynamic diameter increased gradually with α, due to the stretching of the ionized carboxylic groups. However, at higher concentrations, a maximum in R_h was observed, corresponding to α values of ca. 0.25−0.35. Similarly, at this α value, a maximum was observed in the viscosity and a minimum in the scattered light intensity. These results imply that a certain amount of ordering in the solutions exists as a result of repulsive interactions between highly charged micelles. Two well-defined maxima were determined from DLS, corresponding to the collective mode and the diffusion of clusters of structurally organized micelles. Clusters of micelles have also been seen in such aqueous micellar systems as PS-*b*-PEO[67] and Triton X-100.[68]

Solubilization of organic molecules into block polyelectrolytes is a subject of considerable interest due to numerous potential applications. Morishima et al. investigated the quenching of fluorescence probes in hydrophobic domains formed by poly(9-vinylphenanthrene)-*b*-poly(methacrylic acid) (PVPh-*b*-PMAA) in water.[69] The solubilization of organic molecules into aqueous solutions of PS-*b*-PMAA was also followed by fluorescence spectroscopy[61,63] and DLS.[63] Valint and Bock solubilized toluene in block copolymers of poly(*tert*-butylstyrene)-*b*-poly(styrene sulfonate) (PTBS-*b*-PSS) in water and found a corresponding increase in the solution viscosity.[70]

3.2. Characterization of Crew-Cut Micelles. Crew-cut micelles were prepared and characterized from polystyrene-*b*-poly(4-vinylpyridinium iodide) (PS-*b*-P4VPMeI) in water.[71] These micelles consisting of a large hydrophobic PS core and a relatively thin hydrophilic ionic corona (P4VPMeI) were found to be stable and relatively monodisperse. Crew-cut micelles were prepared by dissolving the polymer in DMF and then adding a selective nonsolvent for the PS block. In order to determine the effect of different selective solvents, two procedures were used. In the first, water was added dropwise to the DMF solution; alternatively, methanol was first added, followed by water. In both cases, the solutions were dialyzed against distilled water to remove DMF and methanol. The diameters of the micelle cores were measured by transmission electron microscopy (TEM) and were found to be smaller for the samples prepared by the addition of water, compared with those prepared from water and methanol. Also, the aggregation numbers and polydispersity indexes, calculated from TEM results, were found to be lower for the micelles prepared from the addition of water. The choice of selective solvent is therefore critical to the micellar properties. The higher aggregation number and broader distribution for micelles prepared using methanol and water was attributed to the different compatibility between styrene and water, on one hand, and styrene and a methanol/water mixture on the other.

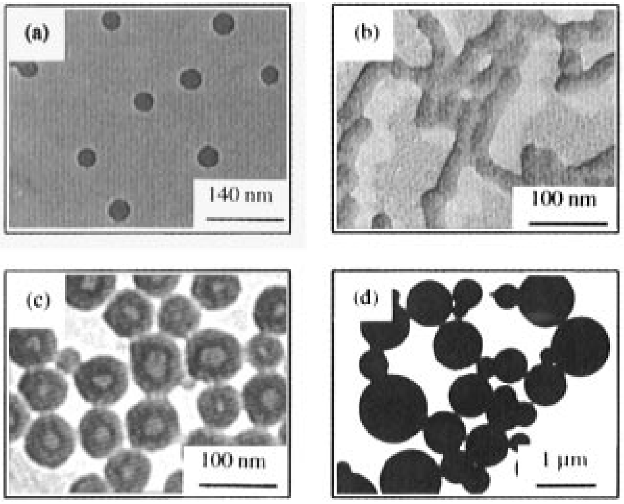

Figure 5. Multiple morphologies of crew-cut aggregates formed from PS-*b*-PAA block copolymers having different compositions: (a) PS(740)-*b*-PAA(55); (b) PS(180)-*b*-PAA(15); (c) PS(200)-*b*-PAA(8); (d) PS(200)-*b*-PAA(4).

Recently, crew-cut micelles were prepared from PS-*b*-PAA in water.[72,73] Different micellar morphologies were observed by TEM depending on the relative block lengths.[73] Typical examples of these structures are shown in Figure 5. Some of these morphologies consist of spheres (a), rods (b), lamellae, and vesicles (c). In addition, compound micelles were observed (d), in which reverse micelle-like aggregates are contained in up to micrometer-size spheres having hydrophilic surfaces. When the samples were dried, ordered needle-like solids formed spontaneously. After soaking in water, the separated needle-like solids showed birefringence under crossed polaroids. This phenomenon may suggest that the solids have crystal-like structure, in which the repeat unit is the micelle particle which is several tens of nanometers in diameter.

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The PS-*b*-PAA spherical crew-cut micelles were characterized in water by TEM and DLS for a wide range of block lengths.[72] The R_c values scaled as $R_c \approx N_{PS}^{0.4} N_{PAA}^{-0.15}$, illustrating an influence of the soluble block length on the R_c values. From DLS measurements, the R_h values were determined, and the thickness and the degree of extension of the coronal chains were estimated from the R_c and R_h values. It was found that the ionized form of the PAA chains (at pH $\approx$ 7) in the coronas had a highly extended conformation. This result was attributed to the charged nature of the PAA chains, the low degree of curvature of the core, and the relatively low concentration of micelles in the DLS experiment.

4. Conclusions

This review has attempted to summarize some recent findings in the field of ionic block copolymer micelles. Both block ionomer micelles and block polyelectrolyte micelles have been characterized extensively by a wide range of techniques. Low cmc's, high micelle stability, and control over aggregate sizes via copolymer composition make ionic block copolymers of interest for a number of possible applications, including drug delivery and materials science. The solubilization of water into the cores of reverse micelles and the preparation of quantum-confined CdS nanoparticles of controlled sizes have illustrated the potential of these systems as microreactors in, for example, the controlled precipitation of metallic and semiconducting clusters. Spherical and nonspherical crew-cut micelles have also been discussed as interesting new morphologies, providing further evidence of the versatility which is offered by solutions of ionic block copolymers.

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