Multiple Morphologies and Characteristics of "Crew-Cut" Micelle-like Aggregates of Polystyrene-*b*-poly(acrylic acid) Diblock Copolymers in Aqueous Solutions

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Received November 3, 1995[⊗]

Abstract: Crew-cut micelle-like aggregates of various morphologies prepared from polystyrene-*b*-poly(acrylic acid), PS-*b*-PAA, diblock copolymers under near-equilibrium conditions, were studied by transmission electron microscopy (TEM). The insoluble block (PS) contents in the copolymers ranged from 80 to 98 wt %. In spherical micelles, the micelle cores, formed by aggregation of the PS blocks, were generally monodisperse. A comparison between star and crew-cut micelles showed that the latter are distinguished by a low density of corona chains on the core surface and a low degree of stretching of the PS blocks in the cores. As the PAA content in block copolymer decreased, the morphology of the aggregates changed progressively from spheres to cylinders, to bilayers (both vesicles and lamellae), and eventually to compound micelles consisting of an assembly of inverted micelles surrounded by a hydrophilic surface. The compound micelles are believed to be a new morphology for block copolymers. The addition of homopolystyrene to the diblocks changed the morphologies from bilayers or cylinders to spheres. The present system provides the first instance in which all these multiple aggregate morphologies have been observed directly in block copolymers in a low molecular weight solvent with changing copolymer composition. It is believed that this is the only way so far to prepare stable nanosize glassy vesicles of block copolymers which form spontaneously and can be isolated in water and studied directly by electron microscopy.

1. Introduction

It has been known for many years that when diblock copolymers are dissolved in a solvent which is selective for one of the blocks, colloidal size aggregates or micelles can form as a result of the association of the insoluble blocks.[1−3] Depending on the composition of the block copolymers, the polarity of the solvent, and the relative solubilities of the blocks in the solvent, the materials can form regular micelle-like aggregates (in aqueous media), which have a hydrophobic core and a hydrophilic corona,[4−9] or aggregates resembling reverse micelles[10−12] when the amphiphilic block copolymers are dissolved in a solvent of low polarity. Because of the range of relative block lengths of most of the block copolymer systems which have been studied to date, either as regular or as reverse micelles, the aggregates have a core which is much smaller than

the corona; such assemblies are sometimes referred to as star micelles. Micelles of another kind, namely crew-cut micelles, have been receiving attention only recently.[13−15] The concept of crew-cut micelles was proposed by Halperin,[16] based on an earlier theoretical study of de Gennes.[17] Crew-cut micelles are characterized by a bulky core and a relatively short corona.

In block copolymer solutions, micelle-like aggregates of spherical geometry have been identified in many studies.[1−15] The structure of a spherical micelle consists of a core of radius R_{core}, formed by the aggregated insoluble blocks of the copolymers, surrounded by a spherical corona shell formed by the soluble blocks. The aggregates take on this spherical geometry in a very broad range of the compositions of the block copolymer.

Nonspherical micelles in solutions of block copolymers have been observed only rarely, and mostly indirectly.[7,14,18−26] On

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⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1996.
(1) Price, C. In *Developments in block copolymers*; Goodman, I., Ed.; Applied Science Publishers: London, 1982; Vol. 1, p 39.
(2) Selb, J.; Gallot, Y. In *Developments in block copolymers*; Goodman, I., Ed.; Applied Science Publishers: London, 1985; Vol. 2, p 27.
(3) Tuzar, Z.; Kratochvil, P. In *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum Press: New York, 1993; Vol. 15, p 1.
(4) Xu, R.; Winnik, M. A. *Macromolecules* **1991,** *24,* 87.
(5) Wilhelm, M.; Zhao, C.-L.; Wang, Y.; Xu, R.; Winnik, M. A. *Macromolecules* **1991,** *24,* 1033.
(6) Prochazka, K.; Kiserow, D.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992,** *25,* 454.
(7) Tuzar, Z.; Kratochvil, P.; Prochazka, K.; Munk, P. *Collect. Czech. Chem. Commun.* **1993,** *58,* 2362.
(8) Astafieva, I.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1993,** *26,* 7339.
(9) Qin, A.; Tian, M.; Ramireddy, C.; Webber, S. E.; Munk, P. *Macromolecules* **1994,** *27,* 120.
(10) Desjardins, A.; Eisenberg, A. *Macromolecules* **1991,** *24,* 5779.
(11) Desjardins, A.; van de Ven, T. G. M.; Eisenberg, A. *Macromolecules* **1992,** *25,* 2412.
(12) Gao, Z.; Desjardins, A.; Eisenberg, A. *Macromolecules* **1992,** *25,* 1300.

(13) Gao, Z.; Varshney, S. K.; Wong, S.; Eisenberg, A. *Macromolecules* **1994,** *27,* 7923.
(14) Honda, C.; Sakaki, K.; Nose, T. *Polymer* **1994,** *35,* 5309.
(15) Zhang, L.; Barlow, R. J.; Eisenberg, A. *Macromolecules* **1995,** *28,* 6055.
(16) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992,** *100,* 31.
(17) de Gennes, P. G. In *Solid State Physics*; Liebert, L., Ed.; Academic Press: New York, 1978; supplement 14, p 1.
(18) Utiyama, H.; Takenaka, K.; Mizumori, M.; Fukuda, M.; Tsunashima, Y.; Kurata, M. *Macromolecules* **1974,** *7,* 515.
(19) Price, C. *Pure Appl. Chem.* **1983,** *55,* 1563.
(20) Zhou, Z.; Chu, B. *Macromolecules* **1988,** *21,* 2548.
(21) Hilfiker, R.; Wu, D. Q.; Chu, B. *J. Colloid Interface Sci.* **1990,** *135,* 573.
(22) Gast, A. P.; Vinson, P. K.; Cogan-Farinas, K. A. *Macromolecules* **1993,** *26,* 1774.
(23) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994,** *27,* 3276.
(24) Zhao, J. Q.; Pearce, E. M.; Kwei, T. K.; Jeon, H. S.; Kesani, P. K.; Balsara, N. P. *Macromolecules* **1995,** *28,* 1972.
(25) Schillén, K.; Brown, W.; Johnsen, R. M. *Macromolecules* **1994,** *27,* 4825.

the basis of light-scattering studies, it was reported that rodlike or cylindrical micelles existed in systems of polystyrene-*b*-poly-(methyl methacrylate) in mixed solvents[18] and polystyrene-*b*-poly(4-vinylpyridine) in dilute solution,[23] depending on the block copolymer composition. Synchrotron SAXS measurements on solutions of polystyrene-*b*-polyisoprene in aniline suggested that vesicles were very probably formed as the content of the soluble polystyrene (PS) block decreased.[20] Very recently, studies of crew-cut micelles from an asymmetric block copolymer, in mixed selective solvents for the short block, also suggested the possible existence of block copolymer vesicles, although that possibility was discounted on the basis of other evidence.[14] The existence of wormlike micelles[19] and of platelet aggregates with copolymer cylinders extending from the edges[22] has been proved by direct TEM observation. Also, regions of stability of spherical and cylindrical micelles in poly(ethylene oxide)-*b*-poly(propylene oxide) triblocks were identified by SAXS and other indirect methods.[25,26]

The existence of various morphologies in block copolymers in bulk has been known for many years. Originally, the three most common morphologies were spherical, cylindrical, and planar/lamellar, depending on the block copolymer composition.[27,28] Later, a new one, the ordered bicontinuous double-diamond or gyroid morphology, was added.[29−32] Multiple morphologies have also been observed in block copolymer/homopolymer blends in bulk.[33,34] Depending on the compositions of the block copolymers and the molecular weight of the homopolymer, the aggregates of copolymers can be spherical, cylindrical, lamellar, and vesicular. Three morphologies (starfish, rod, and planar) adopted by two-dimensional or surface aggregates were observed in polystyrene/decylated poly(vinylpyridinium) block polyelectrolytes within well-defined composition ranges.[35,36] Very recently, three different morphologies, i.e. sphere, rod, and vesicle, have been observed in a polystyrene amphiphilic dendrimer system.[37] Furthermore, it is well-known that small molecule amphiphile surfactant systems form self-assembled aggregates of multiple morphologies.[38−41]

To our knowledge, multiple morphologies of block copolymer aggregates, i.e. spheres, rods, and vesicles or lamellae, have not been observed for the same block copolymer family in solvents of low molecular weight. In a very recent preliminary report,[42] we described the preparation and observation of various morphologies of aggregates made from the diblock copolymers of polystyrene-*b*-poly(acrylic acid), PS-*b*-PAA. Aggregates of several different morphologies were prepared in a low molecular weight solvent system from the block copolymers of the same type differing only in the relative block lengths. Four of these morphologies are spheres, rods, lamellae, and vesicles in aqueous solution. The fifth is new and consists of large spheres in aqueous solution which have hydrophilic surfaces of PAA blocks and are filled with reverse micelle-like aggregates of the copolymers. Regular reverse micelles would, of course, exist in solvents of low polarity. The PS-*b*-PAA system in aqueous solution is believed to provide the first instance in which the existence of all of these aggregates formed from the same block copolymer family in low molecular weight solvents has been proven by direct electron microscope observation. In that report, the preparation of a needle-like solid, which was obtained by drying an aqueous solution of the spherical crew-cut micelles, and which is highly birefringent after soaking in water, was also described.

In the present paper, we present the detailed experimental results concerning the general preparation of the "crew-cut" aggregates and the formation of the various morphologies of the diblock copolymers of polystyrene-*b*-poly(acrylic acid) in low molecular weight solvents. In particular, we report on a range of characteristics of the aggregates and their dependence on the compositions of the block copolymers, as well as on the effect of added homopolystyrene on the morphologies of the aggregates. Finally, a possible mechanism underlying the formation of the different morphologies is discussed.

2. Experimental Section

2.1. Synthesis of the Block Copolymers. The polystyrene-*b*-poly-(*tert*-butyl acrylate) diblock copolymers were synthesized by sequential anionic polymerization of styrene monomer followed by *tert*-butyl acrylate (*t*-BuA) monomer. *sec*-Butyllithium was used as an initiator. Styrene, α-methylstyrene, and *t*-BuA monomers were predried overnight using calcium hydride (CaH₂), distilled under vacuum, and stored under nitrogen at −20 °C. Before polymerization, styrene was treated with fluorenyllithium for 15 min and distilled under vacuum (mechanical pump). *t*-BuA was diluted with toluene and then treated with 10% triethylaluminum solution in hexane until a persistent greenish-yellow color was observed; then, it was distilled under vacuum prior to polymerization. The polymerization was carried out in tetrahydrofuran (THF) at −78 °C under nitrogen gas. α-Methylstyrene was used as the end-capping agent for the polystyryllithium anion. A 5−10-fold excess of LiCl relative to the number of the living anionic chains was added to serve as a stabilizer for the poly(*tert*-butyl acrylate) living end. After the polystyrene block was formed, an aliquot of the reaction medium was withdrawn to obtain a sample of the homopolystyrene polymer for characterization. After the PS was polymerized and end-capped with α-methylstyrene, a series of diblocks with that polystyrene block length was obtained by withdrawing aliquots of the reaction mixtures after each *t*-BuA monomer addition. A more detailed description of the procedures can be found elsewhere.[43]

Gel permeation chromatography (GPC) was used to measure the degree of polymerization and the polydispersity of the polymers. All the homopolystyrenes and their diblock copolymers in the form of *tert*-butyl acrylate gave one narrow GPC peak. The degree of polymerization of the poly(*tert*-butyl acrylate) block was measured by FTIR.[43]

2.2. Hydrolysis. The poly(*tert*-butyl acrylate) block in the block copolymers was hydrolyzed to its acid form, poly(acrylic acid), by using

(26) Glatter, O.; Scherf, G.; Schillén, K.; Brown, W. *Macromolecules* **1994**, *27*, 6046.

(27) Meier, D. J. In *Thermoplastic Elastomers*; Legge, N. G., Holden, G., Schroeder, H. E., Eds.; Hanser: New York, 1987; Chapter 11.

(28) Brown, R. A.; Masters, A. J.; Price, C.; Yuan, X. F. In *Comprehensive Polymer Science: Polymer Properties*; Allen, S. G., Bevington, J. C., Booth, C., Price, C., Eds.; Pergamon Press: Oxford, 1989; Vol. 2, p 155.

(29) Thomas, E. L.; Alward, D. B.; Kinning, D. J.; Martin, D. C.; Handlin, D. L., Jr.; Fetters, L. J. *Macromolecules* **1986**, *19*, 2197.

(30) Hasegawa, H.; Tanaka, H.; Yamasaki, K.; Hashimoto, T. *Macromolecules* **1987**, *20*, 1651.

(31) Thomas, E. L.; Anderson, D. M.; Henkee, C. S.; Hoffman, D. *Nature* **1988**, *334*, 598.

(32) (a) Förster, S.; Khandpur, A. K.; Zhao, J.; Bates, F. S.; Hamley, I. W.; Ryan, A. J.; Bras, W. *Macromolecules* **1994**, *27*, 6922. (b) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063.

(33) Kinning, D. J.; Winey, K. I.; Thomas, E. L. *Macromolecules* **1988**, *21*, 3502.

(34) Bates, F. S.; Kumar, A.; Schulz, M. F. *J. Polym. Sci., Polym. Phys. Ed.* **1995**, *33*, 1423.

(35) (a) Zhu, J.; Eisenberg, A.; Lennox, R. B. *J. Am. Chem. Soc.* **1991**, *113*, 5583. (b) Zhu, J.; Lennox, R. B.; Eisenberg, A. *J. Phys. Chem.* **1992**, *96*, 4727. (c) Zhu, J.; Eisenberg, A.; Lennox, R. B. *Macromolecules* **1992**, *25*, 6547.

(36) Meszaros, M.; Eisenberg, A.; Lennox, R. B. *Faraday Discuss.* **1994**, *98*, 283.

(37) van Hest, J. C. M.; Delnoye, D. A. P.; Baars, M. W. P. L.; van Genderen, M. H. P.; Meijer, E. W. *Science* **1995**, *268*, 1592.

(38) Tanford, C. *The Hydrophobic Effect*, 2nd ed.; Wiley: New York, 1980.

(39) Gruen, D. W. R. *J. Phys. Chem.* **1985**, *89*, 146.

(40) Kaler, E. W.; Murthy, A. K.; Rodriguez, B.; Zasadzinski, J. A. N. *Science* **1989**, *245*, 1371.

(41) Israelachvili, J. N. *Intermolecular and surface forces*, 2nd ed.; Academic Press: London, 1992.

(42) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.

(43) Zhong, X. F.; Varshney, S. K.; Eisenberg, A. *Macromolecules* **1992**, *25*, 7160.

Table 1. Molecular Characteristics of Homopolystyrene and of Polystyrene-*b*-Poly(acrylic acid) Diblock Copolymers

PS-*b*-PAA[a]	M_w/M_n[b]	PS-*b*-PAA[a]	M_w/M_n[b]
170-*b*-33	1.08	500-*b*-58	1.04
180-*b*-15	1.05	630-*b*-18	1.05
180-*b*-28	1.05	705-*b*-22	1.05
200-*b*-4	1.05	740-*b*-55	1.09
200-*b*-8	1.05	740-*b*-180	1.09
200-*b*-15	1.05	1140-*b*-165	1.06
200-*b*-21	1.05	1400-*b*-120	1.08
390-*b*-41	1.06	1400-*b*-306	1.10
390-*b*-79	1.07	PS(38)	1.08
410-*b*-16	1.06	PS(180)	1.05
410-*b*-46	1.06	PS(500)	1.04

[a] Degree of polymerization of the polystyrene from SEC measurements. Poly(acrylic acid) chain length determined by FTIR.[43] [b] Polydispersity index, measured by SEC, of the whole diblock copolymer in the form of PS-*b*-P-*t*-BuA and of the homopolystyrene.

p-toluenesulfonic acid as the catalyst (10 mol % relative to the *tert*-butyl acrylate content). For this procedure, the copolymers were dissolved in toluene, and the solutions were heated at reflux (110 °C) overnight. Finally, after cooling, the block copolymers were precipitated into methanol, washed with methanol several times, and dried overnight under vacuum at 60 °C. FTIR studies[43] showed that the hydrolysis was essentially complete. The polymers are identified by the notation used previously, i.e. PS(180) is homopolystyrene with 180 repeat units (number average). The diblock copolymer samples are denoted as *x-b-y*, where *x* and *y* represent the degrees of polymerization of the PS block and the PAA block, respectively. For example, 200-*b*-4 represents a diblock copolymer containing 200 styrene repeat units and 4 acrylic acid repeat units (number average). The homopolystyrenes and the block copolymers used in this study, along with their molecular characteristics, are given in Table 1.

2.3. Preparation of the Aqueous Solutions. Generally, star type micelles can be prepared directly by dissolving a highly asymmetric block copolymer in a solvent selective for the long block. During the dissolution of the block copolymers, the insoluble (short) blocks form the core while the long blocks form the corona of the micelles. However, because the block copolymers in the present study have a very large weight fraction of polystyrene, it is impossible to prepare stable solutions by direct dissolution of the block copolymer molecules in water. Therefore, in order to prepare stable aqueous solutions, the diblock copolymers were first dissolved in *N,N*-dimethylformamide (DMF), which is a common solvent for both polystyrene and poly-(acrylic acid) blocks. Subsequently, deionized water was added to the polymer/DMF solutions (*ca.* 10 mL) at a rate of 1 drop every 5−10 s with vigorous stirring. As the addition of water progressed, the quality of the solvent for the PS block decreased gradually. The aggregations of the PS blocks of the copolymers, as indicated by the appearance of turbidity in the solution, typically occurred when the water content reached 3−6 wt %, depending on the composition of the block copolymers. The addition of water was continued until 25 wt % of water had been added, i.e. well after the aggregations occurred. The resulting colloidal solutions were placed in dialysis bags and dialyzed against distilled water to remove the DMF. In the present studies, the initial polymer concentration in DMF (before the addition of water) was 2 wt % unless specified otherwise.

2.4. Transmission Electron Microscopy. Transmission electron microscopy (TEM) was performed on a Phillips EM410 microscope operating at an acceleration voltage of 80 kV. For the observations of the size and distribution of the copolymer aggregates, samples were deposited from aqueous solutions (about 0.5 mg/mL) onto copper EM grids, which had been precoated with a thin film of Formvar (J. B. EM Services Inc.) and then coated with carbon. Water was allowed to evaporate from the grids at atmospheric pressure and room temperature. Finally, the grids were shadowed with palladium/platinum alloy at a shadowing angle of about 33°. The sizes of the copolymer aggregates were measured directly from prints of the microscope negatives. For the observation of the internal morphology of the compound micelles, a powder sample of the compound micelles was embedded in epoxy resin (Epon), and sections of about 60 nm thickness

were obtained by microtoming the resin sample at room temperature. In order to increase the contrast between the PAA and the PS regions, the sections were stained with CsOH(aq) and washed with deionized water to remove excess CsOH.

3. Results and Discussion

The Results and Discussion section consists of six parts. In the first, TEM pictures are presented which illustrate the multiple morphologies of the aggregates made from the block copolymers of different compositions. In parts two and three, two characteristics of the crew-cut aggregates are addressed, i.e. the degree of stretching of the PS block in the core region and the surface area per corona chain at the interface of the core/corona shell. These two aspects are thought to be very important in controlling the formation of aggregates. Part four deals with the effect of added homopolystyrene on the morphologies; this is followed by a comparison of multiple morphologies in the present system with those in other systems. Finally, in part six, some additional considerations of the formation of the aggregates are presented.

When block copolymers are dissolved in a solvent selective for one of the blocks, thermodynamic equilibrium may not be operative between the unimers and the aggregates, especially if the glass transition temperature, T_g, of the core-forming blocks is above room temperature. Under those circumstances, the structures should be called micelle-like aggregates (*mlas*). This point is relevant to the present discussion. In the course of preparation of the aggregates in the present system, the copolymers are unimolecular in the DMF before the addition of water. While deionized water is added to the polymer/DMF solution, the solvent becomes progressively worse for the PS block. At a certain water content, the PS blocks start to associate. It appears that there is a true equilibrium between the aggregates and the copolymer unimers at that stage of the aggregation. However, after the formation of the polymer aggregates and subsequent isolation into water, the structures of the aggregates become locked because the PS chains are below their T_g. Thus, they are no longer in thermodynamic equilibrium. Because several of the morphologies described here (with the exception of the vesicles) resemble micelles, and much of the block copolymer literature refers to the nonequilibrium block copolymer mlas as micelles, this convention is adopted in the present work also.

3.1. Various Morphologies of the Crew-Cut Aggregates. 3.1.1. Spherical Micelles. The spherical morphology for crew-cut micelles has been described recently for polystyrene-*b*-poly-(4-vinylpyridinium methyl iodide) in aqueous solutions[13] and for poly(α-methystyrene)-*b*-poly(vinyl-*p*-phenethyl alcohol) (PαMS-*b*-PVPA) in a mixed solvent consisting of *m*-chlorobenzyl chloride and *m*-chlorobenzyl alcohol.[14] In the present systems, the aqueous solutions of the micelles show a pale blue color because of the sizes of the micelles (25−45 nm, see below). The aggregates are readily observable by TEM because of the high T_g of polystyrene, and their sizes are measurable directly from the prints. Most of the block copolymers studied to date yield spherical micelle-like aggregates. Very recently, we reported that the core radii of these spherical micelles have a narrow size distribution.[15] The dimensions of the core radii depend on the chain lengths of both the insoluble (core-forming PS) block and the soluble (corona-forming PAA) block, and scale in the manner of a power law:[15]

$$R_{core} \propto N_{PS}^{0.4} N_{PAA}^{-0.15} \qquad (1)$$

where R_{core} is the core radius, and N_{PS} and N_{PAA} are the degrees of polymerization of the PS and the PAA blocks, respectively.
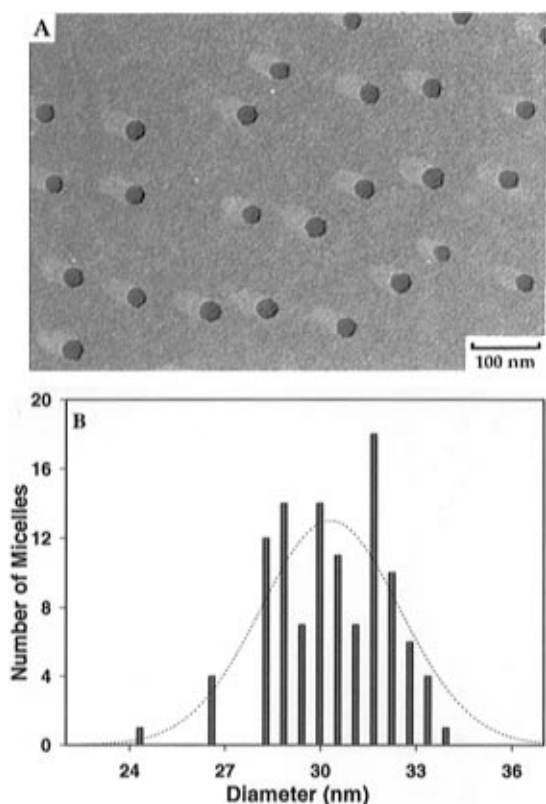
Figure 1. (A) TEM picture of the spherical micelles from the block copolymer 500-*b*-50. (B) The size distribution of the spherical micelles in (A); the dotted line represents a Gaussian fit (average diameter, 30.3 nm, and standard deviation, 2.4 nm).

Figure 1 shows a micrograph of the spherical micelles of a typical sample of the block copolymer, 500-*b*-58, along with a graph of the size distribution which yields an average diameter of 30.3 nm with a standard deviation of 2.4 nm. The dotted line represents a Gaussian fit with the same average diameter and standard deviation. Because the corona-forming block content in the copolymers is low, and because the contrast in the electron density between the copolymer blocks is low, it is not possible to distinguish the micelle corona layer from the core region. However, in view of the composition, it is clear that the corona layer on the core surface must be very thin, and its thickness can be calculated from the composition and the density. In this case, it is 0.3 nm. The observed particle size thus represents the core dimension to a very good approximation. From the size distribution of the micelles, one can readily obtain the average and the standard deviation of the core sizes, the polydispersity index of the micelle molecular weight, etc. The values of these parameters are summarized in Table 2.

3.1.2. Rod-like Micelles. As the block length ratio of PAA to PS decreases, it is found that, below some value of the ratio, the block copolymers associate to form rod-like micelles. Figure 2 shows one example for 180-*b*-15. Most of the micelles appear to be bent rather than straight cylinders. Also, the micrograph suggests a relatively narrow size distribution of the cylindrical micelle diameters, but a widely variable length. Hemispherical caps form at the cylinder ends. The cylindrical micelles are usually found to coexist with aggregates of other morphologies. Preliminary results suggest that the cylindrical micelles are formed only in a relatively narrow range of copolymer compositions. Some characteristics of the cylindrical micelles are listed in Table 3. In the calculations of the surface area per corona chain, the number-average diameters were used, with the lengths of the cylindrical micelles assumed to be infinite.

Table 2. Some Characteristics of the Spherical Micelles

PS-*b*-PAA	PAA (mol %)	D^a (nm)	SD^b ($\pm$ nm)	$A_c{}^c$ (nm^2)	$S_c{}^d$	PI^e (M_w/M_n)
170-*b*-33	16.3	25	1.4	7	1.47	1.02
180-*b*-28	13.5	24	2.2	8	1.38	1.07
200-*b*-21	9.5	26	2.0	8	1.41	1.04
390-*b*-41	12.4	32	3.2	12	1.25	1.09
390-*b*-79	16.8	28	2.4	14	1.13	1.05
410-*b*-46	10.1	30	2.0	14	1.14	1.04
500-*b*-58	10.4	30	2.4	17	1.01	1.04
630-*b*-18	2.8	43	3.8	15	1.32	1.07
705-*b*-22	3.0	41	3.6	17	1.20	1.06
740-*b*-55	6.9	40	2.6	19	1.13	1.03
740-*b*-180	19.6	32	2.4	24	0.90	1.05
1140-*b*-165	12.6	40	2.2	30	0.91	1.03
1400-*b*-120	7.9	42	5.8	34	0.86	1.18
1400-*b*-306	17.9	35	3.4	43	0.72	1.08

[a] Number average diameter of the cores from TEM. [b] Standard deviation of the distribution of the core diameters. [c] Surface area per corona chain at the core/corona interface. [d] Degree of stretching of the PS blocks in the core, taken as a ratio of the core radius to the end-to-end distance of the PS block in the unperturbed state, $(6.76N_{PS})^{0.5}l$, where N_{PS} is the degree of polymerization of PS chain and l is the length of styrene monomer. [e] Polydispersity index of the micelle molecular weight.
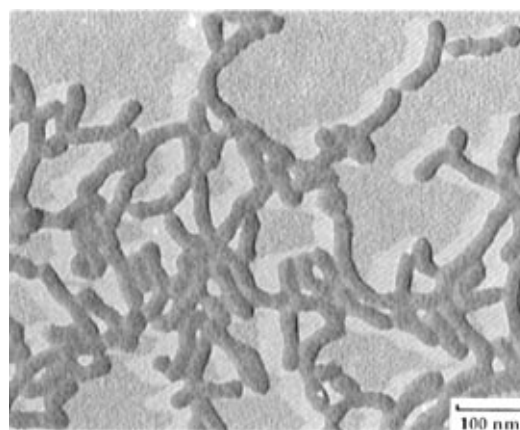

Figure 2. TEM picture of the rodlike micelles from the block copolymer 180-*b*-15.

Table 3. Some Characteristics of the Rodlike Micelles and the Bilayer Aggregates of the Block Copolymers

PS-*b*-PAA	PAA (mol %)	morphology	cylinder diameter or wall thickness^a (nm)	$A_c{}^b$ (nm^2)	$S_c{}^c$
180-*b*-14	7.2	rods	23	5.2	1.32
200-*b*-15	7.0	rods	23	5.8	1.26
410-*b*-25^d	5.9	rods	36	7.5	1.39
200-*b*-8	3.8	vesicles	18	4.2	0.99
410-*b*-20	4.7	vesicles	22	6.3	0.83
410-*b*-16	3.8	vesicles	22	6.6	0.84
410-*b*-16	3.8	lamellae	24	5.7	0.91

[a] Average diameter of the cylindrical micelles or wall thickness of the vesicles. [b] Surface area per corona chain at the core/corona interface. [c] Degree of stretching of the PS blocks; for the cylinder, it is defined as a ratio of the radius to the end-to-end distance of the PS block in the unperturbed state; for the vesicle, half of the wall thickness is used. [d] The initial copolymer concentration in DMF is 2.8 wt %.

3.1.3. Vesicles and Lamellar Micelles. As the ratio of PAA to PS block lengths drops further, vesicular aggregates can form from the block copolymers. Figure 3 shows the morphology of the vesicular aggregates made by the block copolymer 410-*b*-20. The vesicular nature is evidenced from a higher transmission in the center of the aggregates than around their periphery, coupled with height measurements (from shadowing) which show the aggregates to be spherical. The overall sizes of
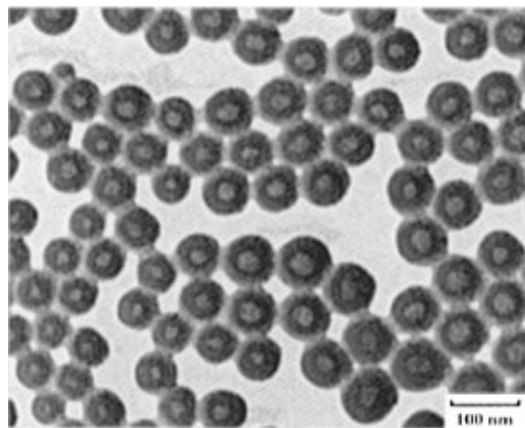
Figure 3. TEM picture of the vesicles from the block copolymer 410-*b*-20.

Figure 4. TEM picture of the compound micelles from the block copolymer 200-*b*-4.

Figure 5. (A) The internal morphology of the large compound micelles in Figure 4. The elongation of the particle shape in one direction is probably caused by the strong shear forces during microtoming. (B) A schematic structure of the large compound micelle filled with bulk reverse micelles. The different degree of darkness of the PAA cores of the reverse micelles represents differences in the degrees of neutralization for different distances from the neutralizing solution.

vesicles are found to be sensitive to the initial copolymer concentration in DMF. For example, the vesicles, formed from 2 wt % 410-*b*-20 copolymer/DMF solution, are quite uniform (Figure 3). For vesicles formed from 3 wt % solution of this copolymer, the sizes are very polydisperse (with the outer diameters ranging from 50 to 500 nm). However, the PS wall thicknesses of the vesicles are very uniform and independent of the overall size of the vesicles. Some structural properties of the vesicles are listed in Table 3. The wall thickness of the vesicles increases with the PS block length.

In examining micrographs of the aggregates in the range of compositions which give vesicles, one also sees lamellar micelles on occasion. The lamellar nature is evidenced by the uniformity of the light intensity over the entire feature. From the measurement of the length of the shadowed region, the thickness of the lamella is found to be the same as the wall thickness of the vesicles in the same picture. This is not surprising because both vesicles and lamellae are bilayer aggregates.

Although it has been known for a long time that some small molecule surfactants form vesicles, the formation of block copolymer vesicles was suggested only rarely and on the basis of indirect evidence. In one case, it was reported[20] that when poly(styrene-*b*-isoprene), PS-*b*-PI, block copolymers were dissolved in aniline, the PI blocks associated to form aggregates. In an analysis of the small-angle X-ray scattering experimental results using different models, it was found that the vesicle model described the experimental system much better than the spherical micelle model for the block copolymer with relatively short PS block length. Very recently, static and dynamic light scattering has been used to study the system of poly(α-methystyrene)-*b*-poly(vinyl-*p*-phenethyl alcohol) (PαMS-*b*-PVPA) in mixed selective solvents.[14] The block copolymer had a composition of [PαMS]/[PVPA] = 90/10 in molar mass. When the solvent is selectively good for the short block (PVPA), the copolymer formed crew-cut micellar aggregates. Because the measured radius of gyration of the core part was much larger than expected, several possible structures of the aggregates were suggested, including vesicles. However, the authors pointed out that the vesicle structure, while possible, was most unlikely for a number of reasons. By contrast to the above reports, the copolymer vesicles in the present study are observed directly and clearly by TEM. Thus, it is believed that this is the first direct observation of the existence of glassy block copolymer vesicles prepared in solution.

3.1.4. Compound Micelles. When the PAA block length becomes very short, it is found that the solutions are extremely turbid. Figure 4 show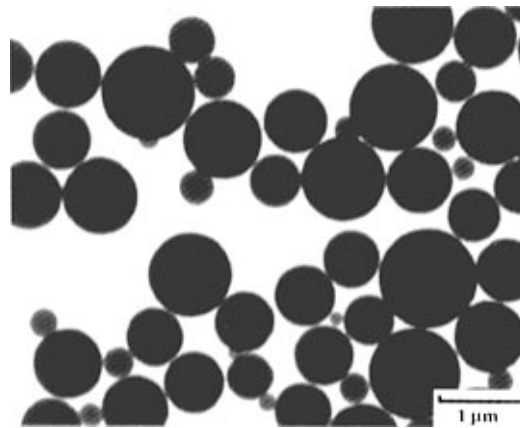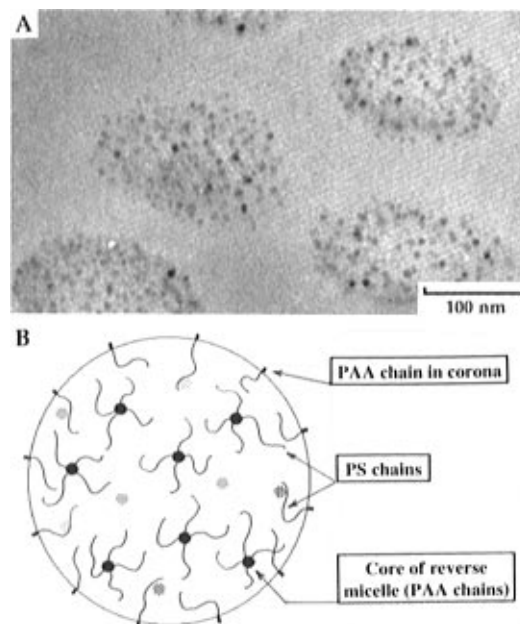s the morphology of the mlas made from the block copolymer with the shortest PAA block length (200-*b*-4). These mlas are solid, highly polydisperse spheres. Because of the very large size of some of these micelles, they are subject to settling due to gravity.

In order to study the internal morphology of these compound micelles, thin sections of about 60 nm were prepared by microtomy at room temperature of specimens embedded in epoxy resin. To increase the contrast between the PAA and the PS regions, the sections were stained with CsOH(aq) and washed with deionized water to remove excess CsOH. A micrograph of a section of the spheres along with a schematic picture (Figure 5) shows that the spheres have a structure similar to that of the block copolymers cast from a solution in a good solvent for the PS blocks, in which the blocks form reverse mlas with the polar cores on the inside and the styrene in the corona. The difference in the degrees of darkness of some of the ionic aggregates (reverse micelle cores) is probably related to difference in the degree of neutralization as consequence of differences in the distances of the aggregates from the surface of the cut. It is likely that the carboxylate groups near the

surface (close to the neutralization solution) may be more completely neutralized than those in the interior. The outer surface of these large compound micelles is hydrophilic because of the presence of the short PAA chains. This gives the micelles considerable stability and allows even those which have settled to the bottom of the container to be resuspended. The micelles do not coalesce at room temperature. We believe that this micellar morphology has not been reported before.

3.2. PS Chain Extension in the Aggregates. 3.2.1. Spherical Micelles. For a compact micelle core, some of the core-forming blocks must span the distance from the core/corona interface to the core center. Therefore, it is of interest to see to what extent the PS chains in the spherical core are stretched in the radial direction compared with their dimensions in the unperturbed state. Because stretching results in a decrease of the entropy of the PS chains, this feature is believed to be important during the formation of the aggregates since it most likely influences the final morphologies.

Table 2 gives the values of the degree of stretching, which is expressed as the ratio of the micelle core radius to the PS chain end-to-end distance in the unperturbed state. Clearly, not all chains are stretched to the same extent, but some must be. Because the end-to-end distance of a polymer chain in the unperturbed state is proportional to square root of the degree of polymerization, $N_{PS}^{1/2}$, the degree of stretching, S_c, can be given by

$$S_c \propto R_{core} N_{PS}^{-0.5} \qquad (2)$$

It is easy to obtain the dependence of S_c on the composition of the copolymers by inserting eq 1 into 2 as

$$S_c \propto N_{PS}^{-0.1} N_{PAA}^{-0.15} \qquad (3)$$

It is clear that the degree of stretching decreases as the PS and/or the PAA block lengths increase. Equation 3 has been used to fit the data of S_c in Table 2. A linear relation is, indeed, found between S_c and $N_{PS}^{-0.1} N_{PAA}^{-0.15}$, with a linear correlation coefficient of 0.96.

The above considerations apply to micelles in aqueous solution. However, it has to be pointed out that, at the moment of the formation of the micelles, the cores are expected to be swollen by the DMF rich solvent mixture. The degrees of stretching of the PS blocks at the onset of micellization are therefore higher than the corresponding values given in Table 2. Since the micelle cores are totally deswelled in aqueous solutions, the degrees of stretching of the PS blocks are decreased. These arguments may explain why some values of the degree of stretching in Table 2 are less than unity.

The degree of stretching is proportional to the dimension of the core region, which, in turn, is determined by the aggregation number (N_{agg}). It has been found that N_{agg} depends on the solvent quality for the blocks of the copolymers.[23] Thus, it is expected that the degree of the stretching should be related to the solvent quality during micellization. At this point, it is useful to introduce the concept of the critical water content (cwc), i.e. the water content at which micelles start to form. At the cwc, PS blocks of the copolymers begin to associate reversibly to form micelles. A study of the phase behavior of polymer/DMF/water systems has shown that the critical water content decreases with increasing PS block length.[44] This means that the copolymers with longer PS blocks form aggregates at a lower water content than those with shorter blocks. From a thermodynamic point of view, the micelles form at values of the χ

(44) Zhang, L.; Eisenberg, A. Manuscript in preparation.

parameter which decrease with increasing PS block length, since water is nonsolvent for the PS blocks.

When the value of χ parameter is relatively low, the core, at the onset of micellization, would be expected to be swollen to a higher degree, which implies a lower volume fraction of the PS blocks in the swollen core region. Given the PS block volume fraction in the swollen core region, f_{PS}, and the radius of the swollen core, R'_{core}, the radius of the unswelled core in the aqueous solutions, R_{core}, can be given as

$$R_{core} = f_{PS}^{1/3} R'_{core} \qquad (4)$$

Equation 4 shows that a lower volume fraction of the PS blocks will give a smaller core size after the core becomes deswelled in aqueous solution. For the copolymer with shorter PS chain length, the micellization occurs at a higher water content. The core is expected to be less swollen compared to that of the copolymers with longer PS chain lengths. A higher polymer fraction in the swollen core will give a larger compact micelle core after the micelles are isolated into aqueous solutions. This may explain, in part, why the degree of stretching of the PS block decreases with increasing PS block length.

3.2.2. Aggregates with Other Morphologies. While the degree of PS chain stretching in the spherical micelle cores is dependent on the composition of the copolymers, it is found that the degree of stretching decreases as the morphology changes from sphere to cylinder, and to vesicle. For example, the block copolymers 200-*b*-21, 200-*b*-15, and 200-*b*-8 have the same PS block and yield, respectively, spherical micelles, cylindrical micelles, and vesicles. The degrees of stretching of PS chains are 1.41, 1.26, and 0.99. If the last two copolymers were to form spherical micelles, the stretching would be expected to increase as PAA block length decreases. According to eq 3, the values of S_c would be 1.47 and 1.62, respectively (rather than 1.26 and 0.99). Thus, the decrease of the degree of stretching accompanying the morphological transitions must be related to the geometric shapes of the aggregates.

The discussion of the effect of aggregate geometry on stretching can start from a consideration of the balance between two relevant contributions to the free energy of micellization, i.e. the surface tension between the core and the solvent, and the stretching force of the PS blocks in the core. From a thermodynamic point of view, an increase of the aggregation number is favored because it decreases the interface area between the solvent and the aggregating blocks. For the case of spherical micelles, the core radius R_{core} has to increase in order to increase the aggregation number. As a result, the degree of stretching of the PS chains has to increase correspondingly, which is thermodynamically unfavorable. For the cylinder, however, the additional degree of freedom along the axis allows many chains to be incorporated into the structure without significant changes in their conformation. The same applies to vesicles and lamallar micelles. Another factor which affects the degree of the PS block stretching may be the interaction between the corona chains, i.e. the repulsion between the corona chains on the surface of the core. This will be discussed in section 3.3.2.

3.3. Area per Corona Chain at the Core/Corona Interface. It has been suggested that the area per corona chain on the core surface is an important factor among those controlling the aggregation number and the structure of the micelles.[9,23] Obviously, a small surface area per corona chain means a lower interfacial energy between the core and the solvent, but a stronger steric repulsion among the corona chains. Thus, it is useful to know the relation between the density of the corona
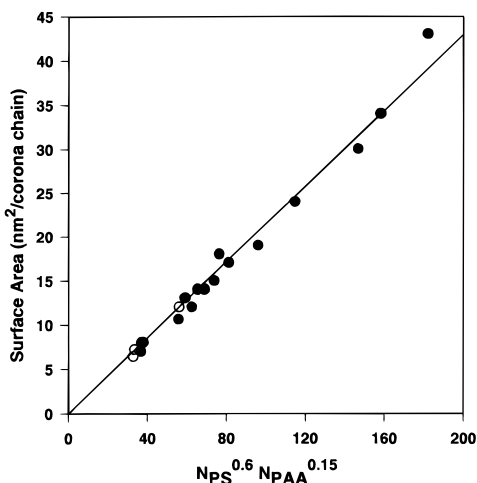
Figure 6. A plot of the surface area per corona chain at the interface of the core/corona shell versus $N_{PS}^{0.6}N_{PAA}^{0.15}$, where N_{PS} and N_{PAA} are the degrees of polymerization of the PS and the PAA blocks, respectively. Open circles represent data from the spherical micelles with added homopolystyrene (*cf.* section 3.4.3.)

chains on the surface of the core, the polymer composition, and the dimension of the PS core region.

3.3.1. Spherical Micelles. For spherical micelles in the present system, the well-defined micelle core sizes determined by TEM allow the calculation of the average surface area per corona chain, A_c. Assuming that the micelle core is a compact sphere and that the density of the polystyrene blocks in the core is homogeneous, A_c is given by

$$A_c = 4\pi R_{core}^2/N_{agg} \tag{5}$$

N_{agg}, in turn, can be calculated as

$$N_{agg} = (4/3)\pi R_{core}^3/V_s N_{PS} \tag{6}$$

where V_s is the volume per polystyrene repeat unit (0.167 nm³). A combination of eqs 5 and 6 yields the relationship between A_c and the core radius as

$$A_c = 3V_s N_{PS}/R_{core} \tag{7}$$

The calculated values of A_c are given in Table 2. For the present system, because $R_{core} \propto N_{PS}^{0.4}N_{PAA}^{-0.15}$, it can be shown that

$$A_c \propto N_{PS}^{0.6}N_{PAA}^{0.15} \tag{8}$$

One can see that A_c increases with PS block length and that, for a constant PS block length, the area also increases as PAA block length increases, although not as strongly. Figure 6 shows a plot of the area per corona chain against the compositions of the copolymers according to eq 8. The linear relationship is clear; the correlation coefficient is 0.98.

For copolymers with a PS block of a constant length, eq 7 implies that the larger the micelle core, the smaller the surface area per corona chain. Obviously, a small A_c can decrease the total surface energy of the micelle core. However, this will be opposed by an increase of the deformation energy of the PS blocks in the core and the repulsive energy between the corona chains. Thus, the final value of A_c will be determined by the force balance among these factors. In the following sections, the effects of the corona-forming and core-forming blocks on A_c will be discussed.

3.3.1.1. Effect of the Core-Forming Block on A_c. In the micelle system of polystyrene-*b*-poly(methacrylic acid) block

copolymers in a mixed solvent of dioxane and water, it was found that the values of the surface area per corona chain fall in a narrow range, which was ascribed to the possible existence of an approximately constant optimum value of that parameter.[9] Furthermore, it was suggested that in micelle formation the interfacial tension between the core and the solvent and the osmotic force acting on the micelle-forming chains balance in a way that maintains a constant interface area per chain.[23] This is clearly not observed in the present crew-cut micelle system. Equation 8 shows how the surface area per corona chain is dependent on the PS chain length in this case. The dependence of A_c on the core-forming block can vary from system to system. However, whatever the dependence of A_c on the insoluble block length, eq 7 must hold. Three cases can be distinguished by considering different degrees of stretching of the PS chains in the core.

First, when the core-forming chain is fully extended, eq 7 predicts that the value of A_c will become independent of the length of core forming chain. An example may be the spherical micelles of small molecule surfactants. In those systems, the surface area per head group is mainly determined by the balance between the surface tension of the micelle core and the repulsion between head groups. Because of the very strong surface tension of the core, the radius of the micelle core is almost equal to the length of hydrophobic chain in the fully extended state, which means tha

$$R_{core} \propto N_C \tag{9}$$

where N_C is the number of carbon atoms in the hydrophobic chain. In practice, it has been shown that the surface area per head group depends mainly on the nature of head group and is almost independent on the hydrophobic chain length. Second, when the degree of stretching of the core-forming block is high, but the chains are not fully extended, eq 7 predicts that a weak dependence exists between A_c and the PS block length. This was, indeed, found to be the case for some star type micelle systems, where the corona-forming blocks are much longer than the core-forming blocks, and the core-forming blocks are highly stretched.[23,45] Last, when the R_{core} is related to N_{PS} by an exponent which is much less than one, the value of A_c will become strongly dependent on the PS block length. This is the case in the present system.

3.3.1.2. Effect of the Corona-Forming Block on A_c. According to eq 8, the surface area per corona chain is also dependent on the soluble block length (N_{PAA}). One possible origin of this dependence may be the steric repulsion between the corona chains, i.e. in cases where the structure of the micelles is mainly determined by the cooperation of the repulsion between the corona chains, the surface tension of the micelle core and the deformation (stretching) of the PS blocks in the core. Obviously, the strength of the steric repulsion between the corona chains is related to the chain density on the surface of the micelle core. Thus, it is essential to know the density of the corona chains. In the studies of polymers adsorbed on solid surfaces,[46,47] a dimensionless parameter, σ, has been used to describe the chain density on the surface. Since similarities exist between grafted polymer chains on a solid surface and corona chains on the surface of a micelle core, it is of interest to use this parameter to explore the density of the corona chains on the surface of the micelle core in relation to various molecular parameters.

(45) Nguyen, D.; Williams, C.; Eisenberg, A. *Macromolecules* **1994**, *27*, 5090.
(46) de Gennes, P. G. *Macromolecules* **1980**, *13*, 1069.
(47) Hadziioannou, G.; Patel. S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.

Table 4. Density of Corona Chains on the Surface of the Core in Several Block Copolymers Micelle Systems

system	type of micelles	solvent	range of soluble block content (mol %)	range of $\sigma N_A^{6/5}$	ref
PS-*b*-PAA	crew-cut	water	4−20	0.2−1.4	present
PS-*b*-P4VP·MeI	crew-cut	water	8−13	0.5−0.9	13[a]
PS-*b*-PMAA	intermediate	80% dioxane/20% water	20−53	0.6−2	9[b]
PS-*b*-P4VP	star	toluene	70−85	13−20	23[c]
PS-*b*-PACs	star	toluene	88−99	12−200	45[d]

[a] Crew-cut micelles made from the polystyrene-*b*-poly(4-vinylpyridinium methyl iodide) copolymers in aqueous solutions. [b] Micelles of polystyrene-*b*-poly(methacrylic acid) copolymers in 80% dioxane and 20% water mixture. [c] Micelles of polystyrene-*b*-poly(4-vinylpyridine) copolymers in toluene. [d] Micelles of polystyrene-*b*-poly(cesium acrylate) in toluene.

σ is defined as the number of terminally grafted chains (corona chains in the present system) per unit area times a^2, where a is the length of the repeat unit ($\sim$0.25 nm for styrene). Thus, its value can be calculated from the equation

$$\sigma = a^2/A_c \qquad (10)$$

When the surface density of the corona chains is low, i.e. the coil domains of the corona chains do not overlap, each chain occupies roughly a hemisphere of radius R_g (the radius of gyration of the corona chain).[46] The low σ region can then be defined by

$$\sigma < a^2/R_g^2 \qquad (11)$$

or

$$\sigma a^{-2} R_g^2 < 1 \qquad (12)$$

Since in a good solven

$$R_g \approx a N_A^{3/5} \qquad (13)$$

where N_A is the degree of polymerization of the corona block, the condition for low surface density of the corona chains can be obtained by inserting eq 13 into eq 12. This yields

$$\sigma N_A^{6/5} < 1 \qquad (14)$$

Equation 14 implies that as $\sigma N_A^{6/5}$ becomes greater than 1, corona chains have to adopt conformations which are extended in the direction perpendicular to the surface due to steric repulsion between the corona chains.

It is interest to calculate the values of $\sigma N_A^{6/5}$ for the spherical micelles of the present system. The results are given in Table 4. For comparison, the values of $\sigma N_A^{6/5}$ for some other systems reported in literature are also calculated and given in Table 4. It is found that the value of $\sigma N_A^{6/5}$ depends on the composition of the copolymers, and generally increases in proportion to the content (mol %) of the corona-forming blocks in the copolymers. For the present system, the values of $\sigma N_A^{6/5}$ fall in the range 0.2−1.4. They are less than unity for most of the micelles, except for three samples with relatively long PAA blocks, where $\sigma N_A^{6/5}$ is slightly higher than unity. This indicates that the surface density of the corona chains is low. It is noted that the values of $\sigma N_A^{6/5}$ are also low in the crew-cut micelles of polystyrene-*b*-poly(4-vinylpyridinium methyl iodide) copolymers in aqueous solutions,[13] as well as in the micelle system of polystyrene-*b*-poly(methacrylic acid) copolymers in the mixed solvent of dioxane and water.[9] However, the values of $\sigma N_A^{6/5}$ are very high for the micelles with relatively long corona-forming blocks,[23,45] implying that the densities of the corona chains are very high on the core surface. In those systems with high surface densities of the corona, the chains are expected to be highly expanded from the core because of the strong steric repulsion between the corona chains. In the last two systems

in Table 4, the core-forming blocks were also found to be highly stretched. As a result, the surface areas per corona chain showed a weak dependence on the lengths of both blocks of the copolymers. For the present system, the steric repulsion between the corona chains is not strong because of the low values of $\sigma N_A^{6/5}$. Thus the value of A_c is mainly determined by the cooperation of two factors, the interfacial tension between the core and the solvent and the force of stretching of the core-forming blocks. As a result, A_c shows a weaker dependence on the length of the corona-forming (PAA) block, but a stronger dependence on the length of the core-forming (PS) block.

3.3.2. Nonspherical Aggregates. It was shown above that for spherical micelles the surface area per corona chain (A_c) depends on the lengths of both the PS and the PAA blocks. In this part, the values of A_c of nonspherical aggregates as well as their relation to the dimensions of the PS regions will be discussed. It is noted that the values of A_c for nonspherical aggregates are lower than those of the spherical micelles (*cf.* section 3.4.3.) and that A_c decreases as the morphology changes from spherical to cylindrical, and to vesicular (Tables 2 and 3). Since morphology changes occur when the length (or content) of the PAA blocks decreases, one of the reasons for the decrease in area can be a shortness of the PAA blocks in the cylindrical micelles and vesicles. However, the geometric shapes of the different morphologies can also play an important role. This is discussed below.

For an aggregate made from copolymers with a constant PS block length, according to eqs 5 and 6, the surface area per corona chain, A_c, is determined by the ratio of surface area to volume of an individual aggregate. An increase in the ratio will increase the surface area per corona chain. For spherical micelles, $A_c = 4\pi R^2/N_{agg}$; since $N_{agg} = (4/3)\pi R^3/V_{chain}$, $A_c \propto 3/R$. Similarly, for cylindrical and lamellar micelles, $A_c \propto 2/R$ and $1/R$, respectively; in the latter case, R is half of the lamellar thickness. Among these different structural aggregates, for a comparable dimension of the PS region (R), the spherical micelle gives the largest value of the surface to the volume ratio. The ratios decrease for different morphologies in the order of sphere, cylinder, vesicle, and lamella. This suggests that nonspherical aggregates will show a lower value of the surface area per corona chain than spherical micelles. Certainly, for each morphology, the value of A_c decreases as the dimension of the PS region (R) increases.

On the basis of the discussion above, one can speculate on the dependence between the surface area per coronal chain (A_c) and the degree of stretching of the core-forming chain (S_c) for the different morphologies. One starts by considering an aggregate with the PS dimension of R. For a spherical micelle, due to a larger surface to volume ratio, and the consequently large exposure of the hydrophobic styrene surface to water, the micelle tends to increase its core size, R_{core}, thus decreasing the value of A_c. The increase of the core size is mainly balanced by an increase of the degree of stretching of the PS blocks. As a result, the PS blocks in the core will be more stretched. However, for nonspherical aggregates, because of a lower

surface to volume ratio, the steric repulsion between the corona chains is increased. The increased steric repulsion will push the corona chains away from each other, which is, in turn, mainly balanced by an increase of the surface tension of the core. As a result, the aggregate will decrease the dimension of the PS block region, for example the wall thickness of the vesicles; the PS chains become more relaxed, and their degree of stretching is decreased. This explains why the PS chains in the spherical micelles are more stretched than that in the cylindrical micelles and the bilayer aggregates (*cf.* section 3.2.2.).

3.4. Effects of Added Homopolystyrene on the Morphologies. It was shown above that the core radius of the spherical micelles depends on the lengths of both the insoluble and the soluble blocks; moreover, as the content of soluble block of the copolymers decreases, the morphology of the copolymer aggregates changes from spheres to cylinders, to bilayers, and eventually to compound micelles. Since the morphology changes as the PS block content in the copolymers increases, it is of interest also to study of the effects of added homopolystyrene on the morphologies.

3.4.1. Relevant Published Studies. In order to understand the effect of added homopolystyrene, it is useful review briefly some of the literature relevant to this topic. Whitmore and Smith[48] in a combined theoretical and experimental study, reported recently on ternary mixtures of homopolystyrene/ polystyrene-*b*-poly(ethylene oxide)/homopoly(ethylene oxide), PS/PS-*b*-PEO/PEO. In that system, the major component is the PS homopolymer, which forms the matrix, while the PEO blocks of the copolymers form spherical micelle cores which are swollen by the PEO homopolymer. That system is of interest because of its similarities to the present system. The authors showed that the number of micelles per unit volume is controlled primarily by the copolymer content. An increase of copolymer content in the mixture increases the number density of micelles per unit volume. PEO homopolymer is solubilized essentially uniformly in the micelle cores up to the solubility limit, which is directly proportional to the existing volume fraction of the PEO blocks of the copolymer in the blends. In contrast to the effect of increasing the copolymer content, the addition of PEO homopolymer only swells the existing micelle cores but does not change their number density or their aggregation numbers. Within the limit of solubilization, all of the added PEO homopolymer is solubilized. Therefore, the following relationship between the core radii before (R_0) and after (R) the addition of PEO homopolymer can be expected:

$$R \cong (1 + \phi_{\text{hPEO}}/\phi_{\text{cPEO}})^{1/3} R_0 \qquad (15)$$

where ϕ_{hPEO} and ϕ_{cPEO} are the volume fractions of PEO homopolymer and PEO blocks of the copolymers in the micelle core, respectively.

It is believed[48] that the solubilization of homopolymer into micelle core is due to the entropy associated with the low homopolymer concentration localized within the micelle core rather than the smaller volume associated with a separate homopolymer phase in the core. The solubilization entropy is opposed by an increase in the stretching of the core forming block as well as the increase in the interfacial energy of the swollen micelles. It was argued that if this were not the case, i.e. if the copolymer relaxed to a less stretched conformation with the homopolymer accumulating towards the centers, the free energy would be minimized by the formation of few very large domains. This would then be a macrophase-separated

system, with the surface decorated by copolymer acting as an emulsifier.[48] Characteristically for this case, the particles would be highly polydisperse.

The study of Whitmore and Smith[48] is confined to aggregates with cores of spherical shape. In our case, we are dealing not only with spherical cores, but also with cores of other shapes, i.e. cylinders and vesicles. Therefore, it would be very useful for the present study to benefit from an investigation of a parallel system to ours, i.e. a system analogous to that of Whitmore and Smith, but involving nonspherical aggregates. Unfortunately, we are not aware of the existence of such a study. However, for binary mixtures of block copolymers (A-*b*-B) and homopolymers (homo-A), or ternary mixtures of A-*b*-B, homo-A and homo-B where the block copolymer is the major component, there are a number of experimental[49−53] and theoretical[54,55] studies, for example, the swelling polystyrene-*b*-polyisoprene (PS-*b*-PI) block copolymers by PS homopolymer. When the PS-*b*-PI copolymers form an alternating lamellar microdomain structure, two possible extreme structures of the mixture can be encountered.[50] In the first case, the PS homopolymer (homo-PS) is located in the PS microdomains of the copolymer. However, the homo-PS chains are not uniformly distributed among the PS blocks and tend to aggregate in the central regions of PS domains. In this case, the average distance between the chemical junctions of PS−PI blocks is not affected at all by the solubilization of homopolymer; the interfaces, on the other hand, move further apart. The other possible extreme is represented by the case in which homo-PS is uniformly distributed among the PS blocks. The uniform solubilization will lead to a conformational change of both the PS and PI blocks. The PS block will tend to expand along the direction normal to the interface. Also, the average distance between the chemical junctions of PS−PI blocks will increase because of the incorporation of homo-PS chains into PS block microdomain. In order to maintain a constant density within the PI microdomain, the dimension of PI microdomain will contract.

Experimentally,[49−52] it was found that when the homo-PS content in the mixture is relatively low, it is essentially distributed throughout the corresponding domains. Although the conformational entropy decreases as a result of chain stretching due to the solubilization of the homopolymer, this entropic penalty can be compensated by the entropy gained from the mixing of the homo-PS and PS block chains. As the homopolymer content in the mixture increases, the lateral expansion of the PS blocks will reach its limit. Beyond that point, the addition of homopolymer induces asymmetric swelling, i.e. the homo-PS chains start to accumulate near the center of PS block microdomain. Thus, the homopolymer concentration profile has a maximum in the center of the PS layer. If the homopolymer content in the mixture increases further, swelling the block copolymers by homopolymers may induce a morphology change of the microdomains, even leading to the formation of an inverted phase. Morphology changes or formation of inverted morphologies are mainly a result of the swelling of the minor block of the copolymer to such an extent that its effective volume per chain is larger than that of the unswollen major block of the copolymer.[53]

(48) Whitmore, M. D.; Smith, T. W. *Macromolecules* **1994**, *27*, 4673.

(49) Hashimoto, T.; Tanaka, T.; Hasegawa, H. *Macromolecules* **1990**, *23*, 4378.

(50) Tanaka, T.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1991**, *24*, 240.

(51) Tanaka, T.; Hashimoto, T. *Macromolecules* **1991**, *24*, 5713.

(52) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1991**, *24*, 6182.

(53) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1992**, *25*, 2645.

(54) Shull, K.; Winey, K. I. *Macromolecules* **1992**, *25*, 2673.

(55) Banaszak, M.; Whitmore, M. D. *Macromolecules* **1992**, *25*, 2757.

Table 5. Some Characteristics of the Spherical Micelles With and Without Added Homopolystyrene

polymers PS-*b*-PAA and PS	composition[a]	experimental diameter[b] (nm)	SD ($\pm$ nm)	calculated diameter[c] (nm)	A_c (nm²/chain)	N_{agg}
500-*b*-58	100:0	30	2.4	30	17	160
500-*b*-58 and 180	95:5	30	2.3	30	18	152
500-*b*-58 and 180	90:10	31	2.2	31	19	164
500-*b*-58 and 180	80:20	36	3.8	32	17	231
500-*b*-58 and 180	70:30	37	9.7	33	16	271
1140-*b*-165	100:0	40	2.2	40	29	180
1140-*b*-165 and 500	90:10	42	3.2	41	30	180

[a] Weight ratio of the block copolymer to the homopolystyrene in the samples. [b] Measured micelle core size from TEM. [c] Calculated micelle core size (eq 15).

3.4.2. Spherical Crew-Cut Micelles. On the basis of the information above, one can explore the behavior of added homopolystyrene in the present system. To incorporate homopolystyrene into the spherical micelle cores, homo-PS was dissolved in the copolymer/DMF solutions before the addition of water. During micellization of the copolymers, the homo-PS solubilized into the micelle core. It was found that the solubilization depends on a number of factors. Most importantly, the homo-PS should have a higher value of the critical water content for precipitation than that of the block copolymer. Otherwise, the homo-PS chains will precipitate first from the solution as the water content increases, without becoming incorporated into the PS core of the copolymer micelle.[44]

Upon addition of homopolystyrene, the block copolymers which form spherical micelles without homo-PS, still yield spherical micelles. Some characteristics of the swollen spherical micelles are given in Table 5. Taking the system of PS(500)-*b*-PAA(58)/PS(180) as an example, one can see that when the weight ratio of homopolystyrene to copolymer is low (<10:90), the micelles are generally monodisperse (standard deviation in the core radius: 6%). The core radius increases only slightly with the addition of homopolystyrene. As the ratio increases to 20:80, the increase of the core radius becomes more pronounced and the core size becomes more polydisperse (standard deviation 11%). When the ratio exceeds 30:70, the sizes of the micelles become even more polydisperse and very large particles start to form in solutions (standard deviation 26%). No morphological transitions are induced by the addition of homopolystyrene.

It is of interest to compare the experimentally determined core radii with those calculated from eq 15. One can see from Table 5 that when the weight ratio of the homo-PS to the diblock copolymer is less than 10/90, the core radii from TEM are in good agreement with the calculated values. The aggregation numbers remain almost constant. These suggest that most of the solubilized homo-PS chains are distributed essentially uniformly in the micelle cores. As the ratio of the homo-PS to the copolymer is increased to 20/80, the experimental core size is appreciably larger than that expected from eq 15. The aggregation number is also increased. This implies that progressively more homo-PS chains accumulate in the core center as the added homopolymer content is increased. The stretching entropy penalty for the PS blocks is reduced as the homo-PS goes to the center. Finally, as the ratio of the homo-PS to the copolymer is increased further to 30/70, very large particles are seen. The very large particles are, very probably, aggregates of homo-PS chains with the surface decorated by the copolymers.

3.4.3. Nonspherical Crew-Cut Aggregates. For the non-spherical aggregates, it was found that the addition of homopolystyrene does change the morphologies, in contrast to the behavior of the spherical micelles. Figure 7 shows that the morphology changes from vesicles to spheres upon the addition of 5 wt % PS(38) homopolystyrene to the 200-*b*-8 diblock. The
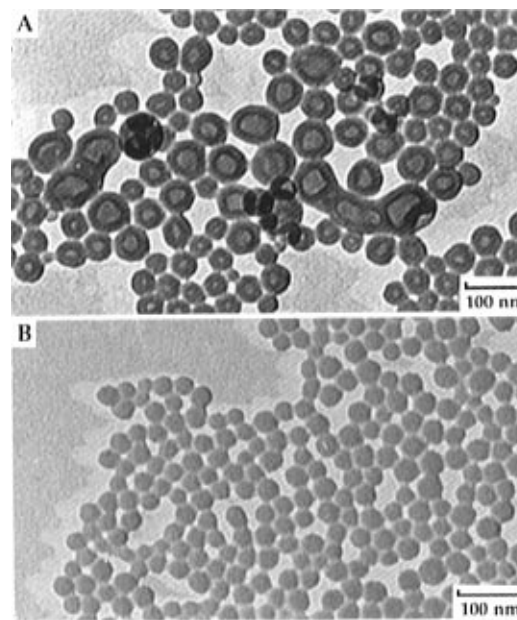

Figure 7. The morphologies of the aggregates formed by the block copolymer 200-*b*-8 (A) without added homopolymer; (B) with 5 wt % of added homopolystyrene PS(38).

morphology also changes from cylinders to spheres by the addition of 5 wt % PS(38) homopolystyrene to the 180-*b*-14 diblock. The characteristics of the aggregates before and after the addition of homo-PS are summarized in Table 6. With the addition of homopolystyrene, the core dimensions of the resulting spherical micelles increase considerably relative to the diameters or thicknesses of the aggregates without added homopolystyrene; however, the polydispersity of the micelles is still low. Because of the low content of homopolystyrene and the low polydispersity of the core sizes of the resulting spherical micelles, it is thought that most of the homo-PS chains are distributed essentially uniformly throughout the cores. Indeed, after the effect of added homopolymer on the core radius is corrected according to eq 15, it is found that the corrected core radii, R_0, of the spherical micelles are in good agreement with the values calculated by the scaling relation found for the present system, $R_{core} \propto N_{PS}^{0.4} N_{PAA}^{-0.15}$ (eq 1). It should be noted that after the morphologies change from nonspherical to spherical the surface area per corona chain increases considerably, implying that the surface area is mostly dependent on the conformation of the PS blocks and the geometric shape of the aggregates, and not primarily on the length of the PAA block itself. The surface area data for these spherical micelles are included in Figure 6 (open circles). It is clear that there is a linear relationship between the surface area and $N_{PS}^{0.6} N_{PAA}^{0.15}$, as suggested in eq 8.

After the morphology changes from nonspherical to spherical, the increased dimensions of the PS regions suggest that the degree of stretching of PS chain may be increased. However, it is possible that the stretching of the PS blocks is not directly

Table 6. Some Characteristics of Originally Nonspherical Copolymer Aggregates with and without Added Homopolystyrene

polymers PS-*b*-PAA and PS	composition[a]	morphology	diameter or wall thickness from TEM (nm)[b]	SD (± nm)	calculated diameter (nm)[c]	S_c[d]	A_c[e] (nm^2)
180−14	100	rod	23			1.32	5.2
180−14 and 38	95:5	sphere	27	1.7	27	1.53	7.2
200-*b*-8	100	vesicle	18			0.99	4.2
200-*b*-8 and 38	95:5	sphere	33	2.8	31	1.79	6.4
410−16	100	vesicle	22			0.84	6.6
410−16 and 180	90:10	sphere	37	2.4	37	1.42	12

[a] Weight ratio of block copolymer to homopolystyrene. [b] Diameter of cylindrical micelles or wall thickness of vesicles. [c] Core diameter calculated from the scaling relation $R_{core} \propto N_{PS}^{0.4} N_{PAA}^{-0.15}$. The effect of the added homopolystyrene on the core size has been corrected by eq 15; the table gives R_0. [d] Degree of stretching of the PS blocks. Definitions are given in Tables 2 and 3.

related to the dimensions of these partly filled spheres because of the possible slight accumulation of some of the homopoly-styrene chains in the core center. A small amount of accumulated homopolystyrene can have a major effect on the deformation of the PS blocks in the core region. This argument can be supported by considering, for example, the mixture of 90 wt % 410-*b*-16 diblocks and 10 wt % PS(180) homopoly-styrene. The resulting spherical micelles have an average radius of 37 nm (Table 6). If all the added homopolystyrene chains were distributed homogeneously in the core, some of PS blocks of the copolymers would need to span the space from the surface to the center of the core. The calculated degree of stretching of the PS block would be about 1.42. However, if only 10% of the added homopolymer were to accumulate in the core center and the rest to distribute homogeneously throughout the entire core region, the degree of the PS block stretching would be reduced to 1.10. The detailed distribution in any particular case would thus involve a balance of the entropic contributions of homopolymer distribution vs chain stretching.

One can speculate about the origin of the dependence of the morphological transitions on the block copolymer composition. Without added homopolymer, as the content of insoluble (PS) blocks in the copolymers decreases, the degree of stretching of the PS block increases (*cf*. eq 3); the change in morphology from spherical to nonspherical can reduce the thermodynamic stretching penalty. With the addition of homopolymer, the morphology change from nonspherical to spherical may be ascribed to two possible aspects. One is the decreased degree of stretching of the PS blocks due to the accumulation of a small amount of homopolystyrene in the center; another is the entropy gained from mixing the homopolystyrene with the PS blocks in the cores.

3.5. Comparison of Multiple Morphologies to Those in Other Systems. The main purpose of this section is to compare the present system to other systems exhibiting multiple morphologies. As mentioned briefly in the Introduction, many examples of multiple morphologies have been observed in micro-phase-separated systems.[27−41] The copolymer/homopolymer blends and small molecule surfactants are of particular interest here because of a range of similarities to the present system; most importantly, both involve a low concentration of aggregating material in a solvent or homopolymer matrix.

3.5.1. Comparison with Copolymer/Homopolymer Blends. For the block copolymer/homopolymer blends, it was reported by Kinning et al.[33] that blending poly(styrene-butadiene) diblocks with a large amount of homopolystyrene results in the formation of a micellar phase consisting of spherical domains of the butadiene blocks. However, the morphology of the butadiene domains can change from spherical to cylindrical and eventually to vesicular, by increasing either the butadiene block content in the block copolymers or the homopolystyrene molecular weight or the volume fraction of the block copolymer in the blends. The major difference between the blend systems

and micelle solutions of the present study is the size of the solvent molecules. By extrapolating the reported trends for the styrene homopolymer to the low molecular weight (i.e. solvent) region, multiple morphologies of block copolymer micelles can be expected only if the block copolymer has a very short soluble block length, with the long block remaining insoluble. This is consistent with the present results, since the morphologically interesting regions occur only for small fractions of soluble blocks in the copolymers. For a typical series of the block copolymers, e.g. 200-*b*-y, as the length of the PAA (soluble) block decreases, the morphology of the formed aggregates changes in the order of sphere (200-*b*-21), cylinder (200-*b*-15), bilayers (vesicle and lamella) (200-*b*-8), and the compound micelle (200-*b*-4).

While the morphology changes as the PAA block contents in the copolymers decrease, it has been observed that the spherical micelles exist in almost all solutions, as evidenced from their presence on a number of micrographs in which other morphologies are dominant. This phenomenon was also found in the copolymer/homopolymer blends.[33] For the present system, the presence of spherical micelles can be explained by one of two possibilities. One may be that, in the process of the addition of water to the polymer/DMF solution, boundaries of stabilities of various morphologies are being crossed, depending on where exactly the region in the phase diagram for a particular morphology was located for a specific run. The phase diagram in the present case is obviously complicated by the multiplicity of factors, i.e. the lengths of both the PS and the PAA blocks, the water content in the DMF, and the total polymer concentration. All of these factors influence the observed morphology. Thus, as water is added, some of the micelles are precipitated, and the polymer concentration changes so that, at some point, a morphological boundary may be crossed.[44] In addition to the above, it should be borne in mind that styrene homopolymer is usually present in the copolymer, because with the addition of *tert*-butyl acrylate monomer during synthesis, some of homopolystyrene chains may have been killed. The presence of homopolymer is known to affect the morphology, as was shown in section 3.4. Thus, since the partitioning of homopolymer into copolymer may be dependent on the total polymer concentration and the water content in DMF, it is entirely possible that the micelles that precipitated first in a particular run have a different homopolystyrene content than those prepared in the late stages of the same run. Thus, it is conceivable that the spherical morphology due to the presence of homopolymer may be favored either in the early or later stages of the micellization run, depending on the relative solubility of the homopolymer in the block copolymer as a function of the relevant parameters.

3.5.2. Comparison with Small Molecule Surfactants. It has been known for many years that aggregates with different morphologies can form in small molecule surfactants systems.[41] The formation of various morphologies is explained in terms

of a dimensionless packing parameter, $v/a_0 l_c$, where a_0 is the optimal surface area of the polar head and v and l_c are the volume and the critical length of the hydrophobic part of the surfactant molecule. The value of the parameter $v/a_0 l_c$ determines the geometry of the aggregates. For example, if $v/a_0 l_c \leq 1/3$, spherical structures are formed. As the value of $v/a_0 l_c$ increases, the morphology of the aggregates can change from spherical to cylindrical, to vesicular and planar, and eventually to inverted spherical.[41] The critical values of $v/a_0 l_c$ for different morphological transitions can easily be obtained by using, for example, the micelle core radius, R_{core}, instead of l_c in $v/a_0 l_c$.[41] Because a_0 is found experimentally to be dependent of the nature of the head group and almost independent on the hydrophobic chain length, and l_c can be estimated from semiempirical equations, the parameter $v/a_0 l_c$ has been used to predict the morphologies of the aggregates successfully. For example, most single-chain surfactants form spherical micelles, while most double-chain surfactants form bilayers because of a higher value of v/l_c.

For the present system, the morphology changes as the length of the corona-forming block decreases. Certainly, as the PAA block length decreases, the surface area per corona chain also decreases. As a result, the value of $v/a_0 l_c$ will increase correspondingly. However, this may not be the primary reason for the morphological changes from spherical to nonspherical as can be seen by considering the balance among a number of forces.

For the micelles of small molecule surfactants, strong repulsion exists between head groups. The surface area per head group is mainly determined by the balance of forces between head group repulsion and hydrophobic attraction of the core surface. Changes in the stretching force of the hydrophobic chains is less important because the chains are stretched already.

For the copolymer crew-cut micelles, the surface area per corona chain is largely dependent on the conformation of the insoluble block (PS) and the geometric shape of the aggregates, not the length of PAA block itself. The repulsion between the corona chains is relatively less important because the blocks are short and acidic. For example, the vesicles formed by the block copolymer 410-*b*-16 have an average surface area of 6.6 nm²/corona chain. However, with the addition of 10% PS(180), the resulting spherical micelles show an average surface area 12 nm²/corona chain (Table 6). It can be argued that if the repulsion between corona chains were the primary factor which determines the value of the surface area, one would not see such a big change in the surface area per chain in going from one morphology to another. Concerning the core regions, the insoluble blocks are essentially random coils and are only stretched to a small extent relative to the end-to-end distance in their unperturbed state. The degree of PS block stretching is a function of the length of PAA blocks. Thus, it is believed that the geometric structures of the aggregates are mainly controlled by the balance of forces between hydrophobic attraction (surface tension) and the stretching of chains in the core-forming block.

3.6. Additional Considerations of the Formation of the Aggregates. 3.6.1. Theoretical Studies of Spherical Micelles in the Literature. Theoretical treatments of spherical block copolymer micelles, pioneered by de Gennes,[17] have been reported extensively in the literature.[56−62] The main goals of

these studies were to find relations between structural parameters of the micelles and the molecular characteristics of the constituent block copolymers using a free energy minimization approach with respect to micellar structure parameters (i.e. the aggregation number or the micelle radius), and then to compare the results of the calculations with the available experimental results.

de Gennes[17] analyzed the formation of diblock copolymer micelles in selective solvent by minimizing the free energy per molecule of an isolated micelle with respect to the aggregation number. Within the framework of that treatment, the free energies of formation of the micellar core/solvent interface and the free energy of stretching of the core-forming blocks control the micellization behavior. On this basis, the treatment predicts that the micelle core radius R_{core} is related the molecular size N_B of the core-forming block as $R_{core} \propto N_B^{2/3}$, when the interfacial energy is large, and as $R_{core} \propto N_B^{1/2}$ when the interfacial energy between the core surface and the solvent is low.

For the formation of diblock copolymer micelles in a homopolymer solvent resulting from the minimization the total free energy of the whole system rather than the free energy of an isolated micelle,[56] Leibler et al. found that for blocks that show weak incompatibility, $R_{core} \propto N_B^{0.53}$. The solvent compatible block was considered to have no influence on the micellar characteristics. Later, a relationship between the core radius and the copolymer composition, $R_{core} \propto N_B^{\alpha} N_A^{-\gamma}$, was obtained by Whitmore and Noolandi,[58] where N_B and N_A represent the degrees of polymerization of the insoluble and soluble blocks, respectively. In their study, qualitative agreement between experiment and theory was obtained for the system of polystyrene-*b*-polybutadiene copolymer micelles in polybutadiene homopolymers. Theoretical values for the exponents lay in the range $0.67 \leq \alpha \leq 0.76$ and $0 \leq \gamma \leq 0.1$, showing that the soluble block had a relatively weak influence on the size of the micelle core.

Nagarajan and Ganesh[61] formulated their theory of micellization of diblock copolymer A-*b*-B in a solvent selective for A on the basis of the multicomponent solution approach similar to that Leibler et al.[56] The Gibbs energy change in terms of standard chemical potential was expressed on the basis of considerations of all relevant physicochemical changes accompanying the transfer of a copolymer molecule from the unimer state to a micelle. They predicted that the soluble block can exert a large influence on the structure of the micelle, particularly in the case of copolymer molecules in which the soluble block is in a good solvent. It was found that the core radius depended on the copolymer composition in the manner $R_{core} \propto N_B^{\alpha} N_A^{-\gamma}$. The values of the exponents, α and γ, depended on the copolymer/solvent system. For polystyrene-*b*-polybutadiene block copolymers in heptane, they found $R_{core} \sim N_B^{0.70} N_A^{-0.08}$; for poly(oxyethylene)-*b*-poly(oxypropylene) copolymers in water they found $R_{core} \sim N_B^{0.73} N_A^{-0.17}$. The larger dependence of R_{core} on N_A in the latter system was attributed to the fact that water is a good solvent for poly(oxyethylene) under the conditions of the measurement.

3.6.2. Spherical Micelles. The present experimental data suggest that the dependence of the core radius on the length of the insoluble block is weaker than that predicted by the theories.[57−61] The difference might be attributable to the conditions under which the micelles form. Generally, the theoretical predictions for the core radius are obtained for a constant value of χ, the interaction parameter of the insoluble block and solvent. However, in the present system, the micelles

(56) Leibler, L.; Orland, H.; Wheeler, J. C. *J. Chem. Phys.* **1983**, *79*, 3550.
(57) Noolandi, J.; Hong, K. M. *Macromolecules* **1983**, *16*, 1443.
(58) Whitmore, M. D.; Noolandi, J. *Macromolecules* **1985**, *18*, 657.
(59) Zhulina, E. B.; Birshtein, T. M. *Vysokomol. Soedin.* **1985**, *27*, 511.
(60) Halperin, A. *Macromolecules* **1987**, *20*, 2943.
(61) Nagarajan, R.; Ganesh, K. *J. Chem. Phys.* **1989**, *90*, 5843.
(62) Munch, M. R.; Gast, A. P. *Macromolecules* **1987**, *21*, 1360.

form and the structures "freeze" at values of χ which decrease with increasing core-forming block length (*cf.* section 3.2.1.).[44] Since the aggregation number should also decrease with decreasing χ, the radius of the core should scale more weakly with the core-forming block length than it does at a fixed χ.

Another reason which may explain the weaker dependence of the core size on the length of the insoluble block can be the value of the surface tension of the core during micellization. Originally, when the block copolymer, PS-*b*-PAA, is dissolved in DMF, the polymer disperses molecularly in the solvent. As water addition progresses, the solvent becomes progressively worse for the PS blocks, until micellization starts at some critical water content. The originally formed micelle cores are probably highly swollen by a DMF rich solvent. The interfacial energy between the core surface and the solvent must be quite low. The low interfacial energy, which is associated with the process of the micellization, is thought to be a very important parameter in the present system. A high interfacial energy will force the micelle to increase its size in order to decrease the surface area per corona chain, the increase in size being balanced by a higher degree of stretching of the core forming block. Accordingly, a low interfacial energy system will result in a weaker dependence of the core radius of the formed micelles on the length of the core-forming block, as predicated by the theoretical study of de Gennes.[17] Finally, the stronger dependence of the micelle core size on the corona-forming block may be ascribed to the stronger interaction (compatibility) between the PAA block and the solvents, with the influence of PAA block becoming relatively more prominent in the system of low interfacial energy.

3.6.3. Nonspherical Micelles. While most of the theoretical studies on block copolymer micellization focus on spherical micelle structures, some papers[62−64] explored theoretically the formation of nonspherical micelles as well as the transition between two different morphologies, e.g. from spherical to rodlike, in terms of changes of the molecular parameters of the polymers, such as the degrees of polymerization of the component blocks of the copolymer and the size of the solvent molecules. Munch and Gast[62] considered the formation of lamellar micelles of block copolymer in solution. It was found that the block copolymer will form lamellar domains in the composition region where the core-forming block is much longer than the corona-forming block. Thus, the lamellar micelles form at copolymer concentrations below the critical micellization concentration found for spherical micelles. Studies also show a significant effect of the size of the solvent molecules on the boundary for the formations of the lamellar and the spherical micelles. Specifically, when the blocks of the copolymers are equal in length, lamellar micelles are favored as the solvent size increases. Mayes and de la Cruz[63] studied cylindrical versus spherical micelle formation in block copolymer/homopolymer blends. A trend toward cylinder formation was observed with increasing core-forming block fraction of the copolymers and increasing homopolymer (solvent) molecular weight. By minimizing the total free energy of a system of micelles, it was found that spherical micelles are precluded because of the higher critical micellization concentration compared to that for cylindrical micelles. Nagarajan[64] studied the shape transitions of block copolymer aggregates. On the basis of the model of an uniform deformation for the copolymer blocks, changes in morphology progressively from sphere to cylinder and to bilayer can be predicated as the insoluble block content increases. While the core dimension of the preferred geometry increases with

increasing insoluble block content in the copolymer, the core dimension is predicted to decrease discontinuously in parallel with the morphology changes. This is qualitatively in agreement with the trend of morphological changes as a function of the block copolymer composition found in the present study.

The major contributions to the thermodynamics of the block copolymer micellization are considered to originate mainly from three sources, i.e. micelle core, the interaction between the corona and the solvent, and the core/corona interface. For the crew-cut micelle system, the contribution of the micellar core and the interfacial tension becomes more important, considering the very short corona block lengths. Thermodynamically, large aggregates are limited for the spherical micelles by the deformation energy of the core-forming blocks. Energy is needed to stretch the copolymer chains from their unperturbed dimensions by confining them to a characteristic micelle geometry. Cylindrical and bilayer aggregates, however, allow more chains to be incorporated into the structure without significant changes in chain configuration. Because of the low interfacial energy between the core and the solvent, the stretching contribution to the free energy appears largely responsible for the transition from spherical to nonspherical micelles. The present experimental results show that the degree of stretching of the PS blocks decreases progressively in parallel with changes of the morphologies from sphere to cylinder and to vesicle.

Because the morphological transitions occur in the composition regions of very low fraction of soluble blocks in the copolymers, it seems likely that, for these very short block lengths, the maintenance of differential solubility may be the crucial factor leading to the formation of the various morphologies. In the present system, it is possible to maintain differential solubility, even for the short blocks, because of the large difference in solubility between the hydrophilic and the hydrophobic segments. Once formed, the aggregates in their various morphologies can be deswelled in water, which makes them very stable because of the strong interactions between the acidic or ionic aqueous corona-forming PAA blocks and water. Also, at room temperature, the deswelled cores are well below the glass transition temperature of bulk polystyrene. The latter feature is certainly helpful, but not essential for stability.

4. Conclusions

Transmission electron microscopy was used to study crew-cut micelle-like aggregates of polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) block copolymers in low molecular weight solvents. The aggregates were formed under conditions of near thermodynamic equilibrium and then isolated into water. Because of the large weight fraction of the PS blocks in the copolymers (from 80 to 98%), the aggregates are readily observable by TEM and their dimensions are measurable from the prints directly.

For spherical micelles, it was found that the micelle cores are generally monodisperse. A comparison between star and crew-cut micelles shows that the latter structures are distinguished by a low density of corona chains on the core surface, and a low degree of stretching of the PS chains in the cores. The core radius (R_{core}), the surface area per corona chain (A_c), and the degree of stretching of the PS blocks in the core (S_c) depend on the copolymer compositions, and scale according to the following relations:

$$R_{core} \propto N_{PS}{}^{0.4} N_{PAA}{}^{-0.15}$$

$$A_c \propto N_{PS}{}^{0.6} N_{PAA}{}^{0.15}$$

$$S_c \propto N_{PS}{}^{-0.1} N_{PAA}{}^{-0.15}$$

These characteristics of the crew-cut micelles result mainly from

(63) Mayes, A. M.; de la Cruz, M. O. *Macromolecules* **1988**, *21*, 2543.
(64) Nagarajan, R. In *Solvents and Self-organization of Polymers*; NATO ASI Series; Webber, S. E., Ed., in preparation.

effects of a low interfacial energy between the core region and the solvent during micellization, as well as the procedures used for the preparation of micelles, as a result of which the values of χ decrease with increasing length of the core-forming block.

As the content of the soluble block (PAA) in the block copolymer decreases, the morphology of the micelles (or aggregates) changes progressively from spheres to cylinders, to bilayers (both vesicles and lamellae), and eventually to compound (inverted) micelles with a hydrophilic surface. The compound micelle is believed to be a new morphology formed by block copolymers in solution. The morphological transitions are believed to be mainly due to changes of the degree of stretching of the PS blocks in the core regions as the block copolymer composition changes.

Homopolystyrene can be solubilized in the core during micellization. The homopolymer chains are generally distributed throughout the core when their content is relatively low. As the content of added homopolystyrene increases, a trend of the homopolymer accumulation in micelle core center can be inferred. The addition of homopolystyrene changes the mor-phologies of the aggregates from bilayers or cylinders to spheres. The change in morphology is ascribed mainly due to the reduced degree of stretching of the PS blocks and possibly the mixing entropy, both of which are associated with the solubilization of the homopolystyrene into the micelle cores.

While various morphologies of the micelles or aggregates of copolymers have been observed in many other systems, it is believed that the present system provides the first instance in which all these multiple aggregate morphologies, i.e. spheres, cylinders, vesicles or lamellae, and large compound micelles, have been observed directly in block copolymers in a low molecular weight solvent with changing copolymer composition. It is also believed that this is the only way so far to prepare glassy vesicles of block copolymers, which form spontaneously and which can be stabilized and isolated in water.