Macromolecules **1995,** *28,* 6055–6066

Scaling Relations and Coronal Dimensions in Aqueous Block Polyelectrolyte Micelles

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Received February 3, 1995; Revised Manuscript Received June 8, 1995[⊗]

ABSTRACT: Polystyrene-*b*-poly(acrylic acid) block copolymers, prepared by sequential anionic polymerization, were found to associate to form spherical, water soluble micelle-like aggregates. The micelle core radii were measured by transmission electron microscopy (TEM). It was found that the core radii scaled as $r_{\mathrm{core}} \sim N_B^{0.4} N_A^{-0.15}$ (where N_B and N_A are the lengths of the insoluble and soluble blocks, respectively), illustrating that the soluble block exerted a considerable influence on the colloidal structure of the micelles. The micellar solutions were also studied by dynamic light scattering (DLS), yielding values of the micelle hydrodynamic radius, r_h. These studies showed that, in the absence of salt, the ionized form of the poly(acrylic acid) chains in the coronal layer of the micelles had a highly extended conformation.

1.0. Introduction

The self-assembly of block copolymers in selective solvents is a phenomenon of considerable interest to a wide range of scientists. The ability of block copolymers to undergo self-assembly in selective solvents imparts them with a number of unique properties, and extensive experimental and theoretical work has been performed over the past two decades. The proliferation of studies in the field has had several impetuses, including the advent of new experimental techniques, which enable the micelle structure to be determined and the micellization phenomenon to be investigated; the development of new theories of micellization; and the recognition that block copolymer micelles may be used in a wide range of industrial and technological applications. The field is reviewed in a number of publications.[1–4]

In a recent paper, we reported on the preparation and characterization of a new type of micelle-like structure formed by the association of block copolymers composed of relatively long polystyrene blocks and relatively short poly(4-vinylpyridinium–methyl iodide) blocks.[5] It was found that the copolymers associated to form spherical micelle-like structures with a polystyrene core and an ionic corona which renders the system water soluble. The description "crew-cut" was applied to these copolymers on account of the fact that the length of the core-forming block was much longer than the length of the corona-forming block. One of the novel features of these colloids was that the micelles had large hydrophobic cores (40–65 nm in diameter) because of the larger number of polystyrene repeat units in the copolymer. Preliminary results indicated that the distribution of core radii was narrow and that the average aggregation numbers and average core radii scaled as a function of the hydrophobic block length, N_B, in a manner predicted by theory.[4]

More recently, we have studied the association of block copolymers composed of long polystyrene blocks and short poly(acrylic acid) blocks. These systems have proven to be extremely interesting, and a number of aspects of their colloidal behavior will be reported in the near future.[6,7] In the present paper, we report on the colloidal structure of spherical micelles formed from these copolymers. In particular, we have studied the relationship between core size and the relative lengths of the polystyrene and poly(acrylic acid) blocks. Furthermore, by measuring the hydrodynamic diameter of the micelles, it was possible to obtain information about the conformation of the poly(acrylic acid) chains in the coronas of the micelles. The major results of this study are that the water soluble poly(acrylic acid) block has a large effect on the micelle formation process and on the structure of the resulting micelles, and that, in the absence of salt, the ionized form of the poly(acrylic acid) chains in the coronal layer of the micelles have a highly extended conformation.

Table 1. Molecular and Micellar Characteristics of Polystyrene-*b*-poly(acrylic acid) Copolymers[a]

copolymer			micelles in water			
N_B(S)	N_A(AA)	(M_w/M_n)	$(r_{\mathrm{core}})_n$/nm	sd/nm	N_{agg}	A_C/nm^2
170	33	1.08	13	0.7	268	7
180	28	1.05	12	1.1	217	8
390	40	1.06	16	1.6	246	13
390	80	1.07	14	1.2	175	15
410	46	1.06	15	1.0	190	14
500	60	1.04	15	1.2	160	17
740	55	1.08	20	1.3	268	19
740	180	1.08	16	1.2	125	24
1140	170	1.06	20	1.1	188	30
1400	120	1.09	21	2.9	159	34
1400	310	1.10	18	1.7	87	43
1400	310[b]	1.10	19	2.0	105	42

[a] The error in N_A and N_B is approximately ±5%; the error in r_{core} is approximately ±1 nm. [b] Prepared by dialysis against deionized water; all other samples were prepared by dialysis against distilled water.

2.0. Experimental Section

Synthesis of Block Copolymers. The anionic polymerization method used to synthesize the polystyrene-*b*-poly(acrylic acid) block copolymers has been previously reported in detail.[8] A complete list of the copolymers studied in this paper is presented in Table 1. In Table 1, N_B is the number of styrene repeat units and N_A is the number of acrylic acid repeat units. In the text, block copolymer samples are differentiated by the notation developed previously; i.e., the copolymer 500-*b*-60 is copolymer containing 500 sytrene repeat units and 60 acrylic acid repeat units. All copolymers had a relatively narrow distribution of molecular weights, with

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[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1995.

0024-9297/95/2228-6055$09.00/0

polydispersity indices (M_w/M_n), estimated by gel permeation chromatography (GPC), in the range 1.04–1.10 (see Table 1).

Preparation of Micelles. Aqueous solutions of the block copolymers were prepared by dialysis. To a solution of the copolymer in DMF (20 cm^3, 2 wt %) was added deionized water at a rate of 1 drop every 10 s. Addition of water was continued until 25 wt % water had been added. The resulting micellar solution was placed in a dialysis bag (Spectra/Por, molecular weight cutoff 8000) and dialyzed against distilled (and, in one case, deionized) water for at least 4 days.

Transmission Electron Microscopy (TEM). TEM was performed using a Phillips EM410 electron microscope operating at an acceleration voltage of 80 kV. Samples were transferred to copper EM grids which had been coated firstly with a thin film of Formvar (J.B. EM Services Inc.) and then with a thin film of carbon. Water was evaporated from the grid over 1 day at atmospheric pressure, and the grids were then shadowed with a palladium/platinum alloy at a shadowing angle of ca. 33°. Number-average micelle core radii $[(r_{core})_n]$, the distribution of core radii $[(r_{core})_w/(r_{core})_n)]$, and the standard deviation of core radii about the mean (sd) were obtained for each sample, by measuring the micelle size directly from prints of the microscope negatives. It was assumed in data analysis that the measured micelle radius corresponded to the radius of the core; i.e., in the dried state, the thickness of the collapsed poly(acrylic acid) corona was negligible in comparison to the core radius. Simple calculations showed that in the extreme case of the sample with the longest poly(acrylic acid) block, 1400-*b*-310, the thickness of the collapsed corona was equal to 6% of the total radius. The accuracy of the microscope magnification was assessed by using a polystyrene latex standard (1.09 μm, Dow diagnostics). The measured number-average core diameter and the manufacturer's quoted number-average core diameter were the same within the error of the measurement.

Dynamic Light Scattering (DLS). DLS experiments were performed on a Brookhaven Instruments Corp. photon correlation spectrometer fitted with a Brookhaven Instruments BI-2030 digital correlator and a Spectra Physics 120 He/Ne laser, which operated at a power of 50 mW and supplied vertically polarized light with a wavelength of 632.8 nm. All experiments were performed at a temperature of 25.0 ± 0.1 °C. The angle of detection could be varied between 35 and 150°, enabling the determination of Γ (s^{-1}) [the relaxation rate of the normalized intensity autocorrelation function, $g_2(\tau)$] over a range of angles. Γ was determined a total of five times, for each angle and concentration, using the single exponential and cumulant methods of data analysis; further details are given in section 3.4.1. From these measurements it was possible to obtain the average *z*-average relaxation rate, $(\bar{\Gamma})_z$.

Great care was taken to ensure that the DLS measurements were not affected by dust. All glassware was cleaned thoroughly with filtered (0.2 μm, × 5), reagent-grade acetone, which had been condensed from the vapor. All solvents and micelle solutions were filtered through surfactant-free, aqueous filters (0.2 and 0.45 μm; Chromatographic Specialties Inc.). Any data which showed the presence of dust were discarded. The concentrations of the micellar solutions were determined gravimetrically after filtration by evaporation of water.

3.0. Results and Discussion

The Results and Discussion section of this paper is organized in the following manner. In the first section (section 3.1), a qualitative discussion of the micelle formation process is presented. The physical conditions which are applicable during copolymer association are discussed, as well as a discussion of the colloidal structure of the resulting micelles. In section 3.2, results obtained by TEM are presented, including the average core radii and the distribution of core radii of different copolymer samples. In section 3.3, the dependence of the core radii on the length of the insoluble block and the length of the soluble block is discussed, using an empirically determined scaling relationship. As part of this discussion, brief comparisons are made between the empirical scaling relation obtained here and a number of theoretical scaling relations.

In section 3.4, results obtained by DLS are presented and discussed. This section includes a brief introduction to the basic theory of DLS (section 3.4.1) and a presentation of the experimental DLS results (section 3.4.2). In section 3.4.3, results obtained by DLS are compared with results obtained by TEM. From this comparison, it was possible to determine the coronal thickness and the degree of extension of the coronal chains for a number of different micellar samples.

In section 3.5, the factors which are known to affect the conformation of polymer chains in the coronas of micelles are discussed. An integral part of this discussion is a comparison of experimental results obtained here with experimental and theoretical results obtained previously by other workers. Section 3.5 begins with a selective summary of the previous literature on the stretching of chains in the coronas of nonionic micelles in organic solvents (section 3.5.1). This section is followed by a discussion of the effect of various parameters on the stretching of coronal chains. The parameters discussed are the following: the effect of the surface density of coronal chains (section 3.5.2); the effect of the curvature of the micelle core to which the chains are attached (section 3.5.3); the effect of the chemical nature of the coronal chains (section 3.5.4); the effect of the quality of the solvent for the coronal chains (section 3.5.4). Finally, in section 3.5.5, a comparison is made between the experimental results obtained here and a number of theoretical and experimental studies of colloids which contain ionic polymer chains attached to the colloid surface.

3.1. Micelle Formation Process and the Structure of the Resulting Micelles. Before presenting specific results, it is necessary to consider the conditions under which the block copolymer molecules associate. It was not possible to prepare stable micellar solutions by direct dissolution of the copolymer molecules into water. This is a consequence of the large weight fraction of polystyrene in the copolymer samples, which renders them insoluble in water. In order to form stable micelles in a completely aqueous environment, it was necessary to first dissolve the copolymer samples in DMF (which is a good solvent for both polystyrene and poly(acrylic acid) blocks) and then gradually decrease the quality of the solvent for the polystyrene blocks by adding deionized water very slowly. Gradual addition of deionized water was continued until 25 wt % of water had been added. Micelle formation, as indicated by turbidity in the solution, typically occurred at 3–6 wt % water addition, i.e., well before dialysis was started. DMF was then removed from the system by dialysis against distilled (and, in one case, deionized) water over a period of at least 4 days.

Under the experimental conditions outlined above, it is reasonable to assume that, in the early stages of water addition, the micelle formation process is a reversible process; i.e., at a given DMF/water concentration, there will be a true equilibrium between the free chain form of the copolymer and the associated form of the copolymer in the micelle. We outline our reasoning below.

All copolymer samples formed clear, molecularly dispersed solutions in DMF. The fact that copolymer molecules were unassociated in DMF was confirmed by light scattering: the molecular weight of the copolymer 500-*b*-60, determined by light scattering in DMF, corresponded to the molecular weight determined by GPC. As the quality of the solvent for polystyrene is decreased further, by adding more water, the solubility of the copolymer decreases and, in order for the free energy of the system to be minimized, association of free chains occurs.

At this stage of the discussion, it is useful to introduce the concept of a critical water concentration, i.e., the concentration of water at which micelles are first formed. At the critical water concentration, different copolymer chains begin to associate reversibly to form micelles, and there is an increase in the turbidity of the solution which can be monitored by light scattering. In a future publication we will present detailed experimental results on the phase behavior of solutions of these copolymers.[7] The various factors investigated in that study include the dependence of the critical water concentration on the polystyrene and poly(acrylic acid) block lengths, the dependence of the critical water concentration on the pH of the precipitating solvent, the dependence of the critical water concentration on the polymer concentration, and an NMR study of the microenvironment experienced by the water molecules during the initial stages of water addition.

At concentrations of water close to the critical water concentration, association of polymer chains is an equilibrium process; i.e., there is a dynamic equilibrium between the single-chain form of the copolymer molecules and the associated form, such that the associated copolymer would become molecularly dispersed if the quality of solvent for the polystyrene blocks were to be improved. Because of the presence of an appreciable amount of DMF in the solution (in the region of 95%), it is expected that the hydrophobic micelle cores will be highly swollen.

As the concentration of water in the solution is increased well above the critical water concentration, the solvent becomes worse for the relatively long polystyrene blocks. As a result, the continuous medium becomes an extremely poor solvent for the free-chain form of the copolymer, and the dynamic equilibrium between the associated form and free-chain form of the copolymer will be shifted in favor of the micelles. The thermodynamics of the system will be such that the lowest free energy state will be the associated state. As the water content is increased further, the micelle core will become less swollen with DMF, and may even become glassy. Once most of the DMF is removed from the system, the micelles will have a kinetically frozen structure; i.e., the copolymer chains will be "locked" into the micelle, and there will no longer by a dynamic equilibrium between micelles and free chains. The frozen micelle structure is a consequence of the strong hydrophobic interaction between different polystyrene chains, the relatively high glass transition temperature of polystyrene, and the low solubility of the copolymer in water. Furthermore, once the micelle has been transferred to a completely aqueous solvent, it is reasonable to assume that the polystyrene core will not be swollen with solvent.

One aspect of this micellization process that needs to be addressed is at which stage of water addition a transition from an equilibrium micelle system (an associate) to a nonequilibrium system (an aggregate) occurs. If the micelle structure becomes frozen instantaneously at one equilibrium state, then the structure of the micelles in the frozen state will reflect the structure of the micelles in that equilibrium state. However, the instantaneous freezing of micelles may not be entirely realistic. For example, during the addition of water, there may be a change in the kinetics of micellization, which is a consequence of the progressive removal of DMF from the micelle core with increasing water content. Therefore, it is possible to propose that as more and more solvent is leached from the micelle core, there will be a gradual slowing down of the rate of micellization. Therefore, as the water content is increased, there is a simultaneous change in the kinetics of micellization and the thermodynamics of micellization. If the rate of micellization approaches, or becomes slower than, the rate at which the equilibrium constant changes with the addition of water, then it will no longer be possible for the micellar solution to adjust to a new equilibrium state. In this situation, we would expect that the final frozen structure of the micelle will be a function of the change in the micellization kinetics, along with the state of the micelle equilibrium near the freezing point.

Table 2. Micelle Hydrodynamic and Structural Information[a]

sample	pH	$[(1/r_h)_z]^{-1}$/nm	$[(1/r_h)_z]^{-1} - (r_{core})_z$/nm	extension/%
500-*b*-60	6.6	23	9	60
1140-*b*-170	7.0	52	32	75
1400-*b*-120	7.1	50	29	97
1400-*b*-310	6.8	90	72	96
1400-*b*-310[b]	4.5	38	20	25
1400-*b*-310[c]	5.3	48	30	39

[a] The error in r_h is approximately ±5%; the error in r_{core} is approximately ±1 nm. [b] Prepared by dialysis against deionized water; all other samples were prepared by dialysis against distilled water. [c] NaCl was added to this sample; total concentration of NaCl equaled 1.0 mol dm^{-3}.

We are, at present, attempting to resolve the question of what conditions pertain during micellization using various quenching techniques. The determination of the actual thermodynamic and kinetic conditions which are operative, at the point at which the micelle structure becomes frozen, may be a difficult task. We have not attempted to resolve this question in the present study. We do, however, note two things associated with this aspect of the work. Firstly, at most stages of the micelle formation process, the associated copolymer molecules were equilibrium micellar associates; we use the word micelle to describe the final frozen aggregates because of this fact. Secondly, the distribution of core radii in the final micellar solutions is narrow (see section 3.2). This fact indicates that relatively few micellization equilibria are operative at the point at which the micelle structure becomes frozen. One fortunate aspect of the frozen structure of these micelles, from an experimentalist's viewpoint, is that systems of this type are readily characterized; i.e., their aggregation number is fixed and not influenced by dilution, or by changing the temperature below the glass transition temperature of the polystyrene block.

Of importance to the second part of this study is the extent of neutralization of the poly(acrylic acid) chains in the coronal layer of the micelles. As mentioned in section 2.0, most samples were dialyzed against distilled, but not deionized water. The pHs of the resulting micellar solutions after dialysis were in the region 6.5–7.1 (see Table 2). From literature data on the acid–base behavior of poly(acrylic acid)[9,10] it is possible to estimate that the degree of ionization (α) of the poly-

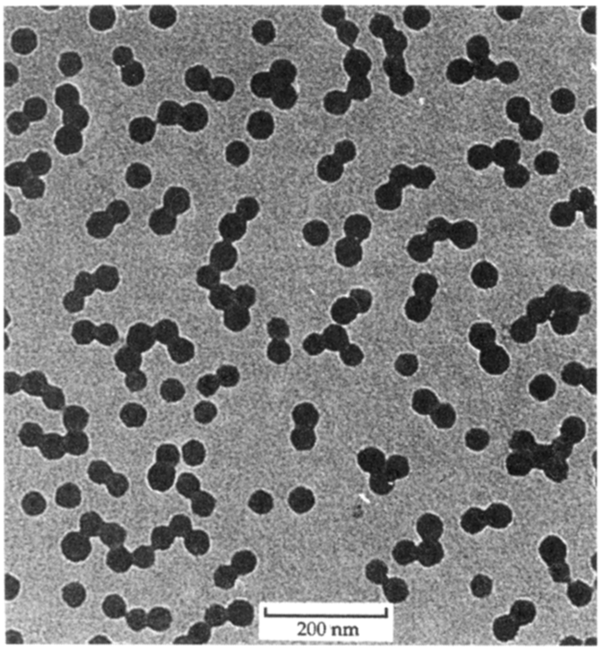

Figure 1. Transmission electron micrograph showing micelles formed from the copolymer 1140-*b*-170. The scale bar on the micrograph print shows 200 nm.

(acrylic acid) chains in the coronas of these micelles is in the region $0.8 > \alpha > 0.5$. The high pHs of the micellar solutions suggest a process of cation exchange during the extended dialysis. This ion exchange, between cations in the distilled water and protons on the polymer chain (obviously subject to a Donnan equilibrium), produces neutralized polyelectrolyte chains in the coronas of the micelles. That cation exchange occurs during extended dialysis against distilled water can be corroborated by the fact that a micellar solution of the polymer 1400-*b*-310, prepared by dialysis against deionized water, had a pH of 4.5.

It is reasonable to assume that cation exchange occurs after the micelles have been formed and that the polymer chains in the corona do not become charged until after the micelle structure has been established. It is thus assumed that neutralization of the polymer chains does not influence the micelle formation process. This assumption is upheld by core radius measurements (see Table 1). The average core radii of micelles formed from the polymer 1400-*b*-310 in distilled and deionized water were essentially identical (18 and 19 nm, respectively) even thought the pHs of the micellar solutions were, respectively, 6.8 and 4.5.

3.2. Distribution of Core Radii. All of the copolymer samples prepared in this study associated to form completely spherical micelle-like structures. A typical micrograph of micelles formed from the copolymer 1140-*b*-170 is presented in Figure 1. The use of electron microscopy to measure micelle core radii directly alleviates many of the problems associated with the use of other methods of measuring core radii, such as small-angle X-ray scattering (SAXS). For example, in order to obtain the core radius it is not necessary to use any particular theoretical model to fit the experimental data. The number-average core radii [$(r_{\mathrm{core}})_{\mathrm{n}}$] of the different copolymer samples are presented in Table 1, along with the standard deviation of core radii about the mean (sd), and the aggregation numbers (N_{agg}) calculated from the core radii, assuming an unswollen core. It is clear that the majority of samples had a relatively narrow distribution of micelle core radii, with standard deviations from the mean (sd) in the range 0.7–2.9 nm (5–14%).

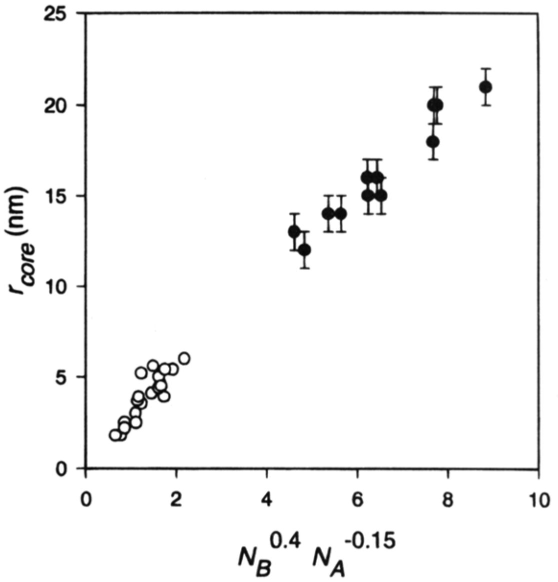

Figure 2. Plot of average core radius (r_{core}/nm) versus $N_{\mathrm{B}}^{0.4}N_{\mathrm{A}}^{-0.15}$ for different micelle systems. N_{B} is the length of the insoluble block, and N_{A} is the length of the soluble block. Filled circles are number-average data for polystyrene-*b*-poly(acrylic acid) micelles in water obtained by TEM. Open circles are weight-average data obtained by Nguyen et al. using small-angle X-ray scattering[20] to study polystyrene-*b*-poly(cesium acrylate) and polystytrene-*b*-poly(4-vinylpyridinium–methyl iodide) reverse micelles in toluene.

3.3. Dependence of the Core Radii on the Length of the Insoluble Block (N_{B}) and the Length of the Soluble Block (N_{A}). One of the goals of this work was to compare experimentally determinable quantities (e.g., number-average core radii, aggregation numbers, and hydrodynamic radii) with the predictions from the various scaling theories which are now in place.[4,11–17] Because of the versatility of the copolymer synthesis and the relatively large range of samples, it was hoped that the effect of the length of the polystyrene and poly(acrylic acid) blocks on the micelle structure could be investigated in detail. It should be noted, especially in relation to section 3.1, that the micelles studied here are nonequilibrium structures. However, the micelles were formed under equilibrium conditions, and as such the structure of the micelles should reflect the structure which pertained under equilibrium conditions. This study is in the spirit of an earlier study by Qin et al., in which the aggregation numbers and hydrodynamic diameters of micelles, formed from a relatively wide range of polystyrene-*b*-poly(methacrylic acid) copolymers in a water/dioxane mixture, were investigated.[18]

It was found that none of the theoretical scaling relations used, nor a variety of empirical scaling relations[18,19] could scale the core radius and aggregation number data cleanly. In particular, it was found that those scaling relations in which only the length of the insoluble block is considered to influence the structure of the micelle could not be used to scale the data. Therefore, in order to scale the average core radii data, we had to fit the data empirically. The results of this finding are shown in Figure 2, where the measured number-average core radii are plotted against $N_{\mathrm{B}}^{0.4}N_{\mathrm{A}}^{-0.15}$. The value of the exponents was determined by trial and error: the values were altered relative to each other and the combination which gave the best linear regression fit to the experimental data (+0.4 and −0.15) was chosen.

Included in Figure 2 are weight-average core radii for block ionomer micelles in toluene, obtained by Nguyen et al.[20] using small-angle X-ray scattering (open circles). These copolymers are composed of a polystyrene block and either a poly(cesium acrylate) or poly(4-vinylpyridinium–methyl iodide) ionic block and aggregate in organic solvents to form reverse micelles with ionic cores. From Figure 2, it is clear that there is a linear relationship between the core radius and $N_B^{0.4}N_A^{-0.15}$ for both sets of data.

We do not consider the scaling relation obtained here to be universal in nature. The fact that the core radii data from these two very different micellar systems scaled well with $N_B^{0.4}N_A^{-0.15}$ may illustrate that the various energy contributions for the different copolymer/solvent systems balance in a way to lead to an apparent similarity in the numerical value of the exponents. The proposition that the dependence of r_{core} on N_A and N_B may be system specific is corroborated by the fact that we could not use the empirical scaling relation obtained here to scale cleanly the weight-average core radii data obtained by McConnell et al.[21] The core radii of polystyrene-*b*-polyisoprene micelles in decane, obtained by McConnell et al. using small-angle neutron scattering (SANS), are to the best of our knowledge, the only other comprehensive data on the dependence of the core radii on the length of the soluble and insoluble blocks, other than those presented here. We found that the data of McConnel et al. did not fit our empirical scaling relation in a quantitiatve sense; i.e., the measured core radii did not coincide exactly with the data points shown in Figure 2. However, it was found that their core radii data did show a soluble block dependence. In particular, we found that their data scaled better when the length of the soluble block was considered.

While it is recognized that the empirical scaling relation obtained here is not applicable to every block copolymer/solvent system, our results do illustrate that the micelle core radius depends on both the length of the insoluble block and the length of the soluble block, scaling in the manner:

$$r_{\text{core}} \sim N_B^{\alpha} N_A^{-\gamma}$$

The fact that samples of very different chemical composition (which associate in very different solvent media) show a linear relationship between the average micelle core radii and a quantity of the type $N_B^{\alpha}N_A^{-\gamma}$ suggests that the soluble block plays a role in the micelle formation process and influences the structure of the resulting micelles. This further suggests that in any theoretical treatment of the micellization of block copolymers the influence of the soluble block should be considered.

Theoretical expressions relating the core radius to a quantity of the type $N_B^{\alpha}N_A^{-\gamma}$ were first obtained by Whitemore and Noolandi using a free energy minimization approach.[14] Their theory is based on micelle formation in block copolymer–homopolymer blends and was applied specifically to experimental data obtained on polystyrene-*b*-polybutadiene copolymer micelles dissolved in polybutadiene homopolymers. In their study, qualitative agreement between experiment and theory was obtained. Theoretical values for the exponents lay in the range $0.67 \leq \alpha \leq 0.76$ and $0.1 \leq \gamma \leq 0$, showing that the soluble block has a relatively weak influence on the size of the micelle core. This conclusion is in contrast to the theory of Nagarajan and Ganesh.[17] 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. Generalized scaling relations were developed for r_{core} and N_{agg}, as well as the molecular properties of the solvent and copolymer. To facilitate quantitative calculations, two model systems and three specific block copolymer/solvent systems were chosen. They scaled the data in terms of the effective number of repeat units, m_B and m_A [$m_B = (N_B V_B/V_s)$, where V_B and V_s are the molecular volume of the insoluble copolymer block repeat unit and solvent, respectively]. The values of the exponents which they obtained depended on the copolymer/solvent system. For polystyrene-*b*-polybutadiene block copolymers in heptane they found $r_{\text{core}} \sim m_B^{0.70}m_A^{-0.08}$; for poly(oxyethylene)-*b*-poly(oxypropylene) copolymers in water they found $r_{\text{core}} \sim m_B^{0.73}m_A^{-0.17}$. 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. Zhulina and Birshtein[15] also proposed an expression for r_{core} in a specific copolymer composition region, roughly corresponding to the composition of the polystyrene-*b*-poly(acrylic acid) copolymers studied here, in which the micelle core radius scaled as $N_B N_A^{-\gamma}$. The value of γ depended on the quality of the solvent, being equal to 0.5 in a Θ solvent and equal to 0.545 in a good solvent.

The basic difference between our empirical fit and the theoretical expressions of Whitemore and Noolandi, Nagarajan and Ganesh, and Zhulina and Birshtein is quantitative; i.e., the experimental values of the exponents are different from the theoretical values. In particular, our experimental data suggest that the dependence of the core radius on the length of the insoluble block is weaker than predicted by theory. The difference in the value of the exponents obtained here from those predicted by theory is probably due to the interplay of several different contributions. As already mentioned, differences in the physicochemical nature of the specific interactions in different block copolymer/solvent systems may lead to different values of the exponents. Differences in the manner in which block copolymer systems associate may also be of importance. For example, it has been noted that in order for equilibrium micellar structures to be formed it is necessary to ensure that micelles associate under conditions in which there is a dynamic equilibrium between the free-chain form of the copolymer and the associated micellar form.[22] Furthermore, most theoretical predictions of the core radius r_{core} are obtained for a constant value of the interaction parameter, χ. However, in present system, the values of χ at which the micelles formed were to decrease with increasing N_B; then the values of r_{core} may scale more slowly with N_B than at fixed χ. Finally, the influence of experimental error on the values of the exponents should not be underestimated. For example, in their study Whitmore and Noolandi[14] estimate that an uncertainty of ±0.2 nm in the measured values of r_{core} produced an uncertainty of $\sim\pm 0.05$ in γ and $\sim\pm 0.1$ in α. At this point of our study it is not clear whether there is a discrepancy between experiment and theory or an agreement. Future work with other copolymer systems or different procedures for the micelle preparations may help resolve this question.

3.4. Investigation of the Micelle Structure by DLS. 3.4.1. Basic DLS Theory. The basic quantity measured in the DLS experiment is the intensity autocorrelation function, $G_2(\tau)$, which, in a dilute solution of monodisperse particles, is an exponentially decaying function of the decay time, t (s). $G_2(\tau)$ is related to the normalized electric field autocorrelation function, $g_1(\tau)$, via the Siegert relationship:

$$G_2(\tau) = B(1 + \beta|g_1(\tau)|^2) \qquad (1)$$

where B is the measured baseline of the decaying autocorrelation function and β is the coherence factor which can be used as an adjustable parameter in the data analysis. In the simplest case of monodisperse noninteracting particles, $g_1(\tau)$ is a simple, single exponential function:

$$g_1(\tau) = \exp(-\Gamma\tau) \qquad (2)$$

where Γ is the relaxation rate of the decaying autocorrelation function (s^{-1}). Γ is related to the diffusion coefficient, D ($m^2\ s^{-1}$), by

$$\Gamma = Dq^2 \qquad (3)$$

where q is the scattering vector:

$$q = (4\pi n/\lambda)\sin(\theta/2) \qquad (4)$$

Here n is the refractive index of the scattering medium (water), λ is the wavelength of the incident light (m), and θ is the scattering angle.

It is often found that the experimental autocorrelation function is not a single exponential function and that there is a distribution of relaxation rates. The analysis of experimental data in these circumstances can become much more complicated and is, in many respects, a developing field. Various methods of data analysis have been developed; a review of the field is given by Štêpánek.[23] In the present study, data were fitted by a single exponential method and by the method of cumulants developed by Koppel,[24] using the Brookhaven correlator software. Because of the more reliable fitting of the experimental data by the cumulant method, all subsequent quantitative analyses were performed using values of the mean z-average relaxation rate $(\bar{\Gamma})_z$ obtained by this technique.

In the method of cumulants the correlation function is expanded about a z-average relaxation rate, $(\bar{\Gamma})_z$. The result is a polynomial expansion in the sample time with cumulants (moments about $(\bar{\Gamma})_z$) as the parameters to be fitted. For polydisperse, pointlike, isotropic particles without intermolecular interactions the expansion may be written

$$|g_1(\tau)| = \exp\{-\bar{\Gamma}\tau + (\mu/2!)\tau^2 + ...\} \qquad (5)$$

where $\bar{\Gamma}$ is the intensity (I)-weighted mean relaxation rate, sometimes referred to as the initial slope $[\bar{\Gamma} = \sum_i I_i(\Gamma_i - \bar{\Gamma})]$, and μ is the second moment of the distribution of the relaxation rates about the mean $[\sum_i I_i(\Gamma_i - \bar{\Gamma})^2]$. The logarithm of eq 5 can be fitted by a non-negative least squares routine. The ratio $\mu/(\bar{\Gamma})_z^2$ is a measure of the width the intensity distribution of relaxation rates, which can be used to give an indication of the polydispersity of the sample under investigation.

3.4.2. DLS Results. In the present study, all micelle samples gave values of $\mu/(\bar{\Gamma})_z^2$ in the range 0.07–0.20, illustrating that there was a distribution of relaxation rates contributing to the correlation function. These results also suggest that a more sophisticated data analysis technique, such as the CONTIN method due to Provencher,[25] should be used to extract information on the distribution of relaxation rates. It should be noted that correlation curves obtained in the present study were exponential and did not have any biexponential character. Therefore, we feel that the polydispersity observed in the concentration ranges studied here is due mainly to polydispersity in micelle size, rather than to the formation of ordered structures in solution (as has been previously observed for ionized polystyrene-*b*-poly(methacrylic acid) micelles[26]) or because of strong electrostatic interactions between micelles.[27] This assertion is corroborated by the fact that the sample 1400-*b*-310, which was prepared by dialysis against deionized water, also exhibited appreciable micelle polydispersity by DLS. This sample should have the lowest degree of ionization of all samples and therefore should be least affected by strong electrostatic intermicellar interactions. A number of explanations can be proposed for the observed polydispersity in micelle size. For example, the micelle polydispersity may be due to compositional polydispersity in the corona-forming blocks. However, we prefer to await results obtained by the CONTIN method before discussing this observation further. These studies are currently underway in our laboratory.

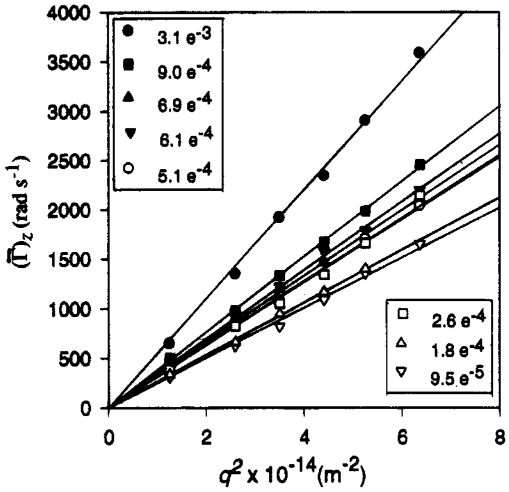

Figure 3. Plot of the average z-average relaxation rate [$(\bar{\Gamma})_z$/rad s^{-1}] versus the square of the scattering vector (q^2/m^{-2}) for different concentrations of micellar solutions of the block copolymer 1400-*b*-310. The concentrations shown are (●) 3.1 × 10^{-3} g cm^{-3}, (■) 9.0 × 10^{-4} g cm^{-3}, (▲) 6.9 × 10^{-4} g cm^{-3}, (▼) 6.1 × 10^{-4} g cm^{-3}, (○) 5.1 × 10^{-4} g cm^{-3}, (□) 2.6 × 10^{-4} g cm^{-3}, (△) 1.8 × 10^{-4} g cm^{-3}, and (▽) 9.5 × 10^{-5} g cm^{-3}.

Angular dependence data obtained on the present micellar solutions also suggest that strong intermicellar interactions did not influence the DLS results. Data for micelles formed from the sample 1400-*b*-310, prepared by dialysis against distilled water, are shown in Figure 3. The pH of this sample was 6.5, illustrating that the acid groups in the coronal layers of the micelles were ionized. The different plots of $(\bar{\Gamma})_z$ versus q^2 are straight lines which, within the variation of $(\bar{\Gamma})_z$, pass through the origin. This illustrates that the relaxation mode was diffusive in nature; i.e., free diffusion of the micelle was investigated in the concentration range studied. The simple angular dependence of the measured relaxation rate suggests that long-range interactions were not probed in the experiments.

From the slopes of the plots of $(\bar{\Gamma})_z$ versus q^2, it is possible to obtain a value of the diffusion coefficient, D.

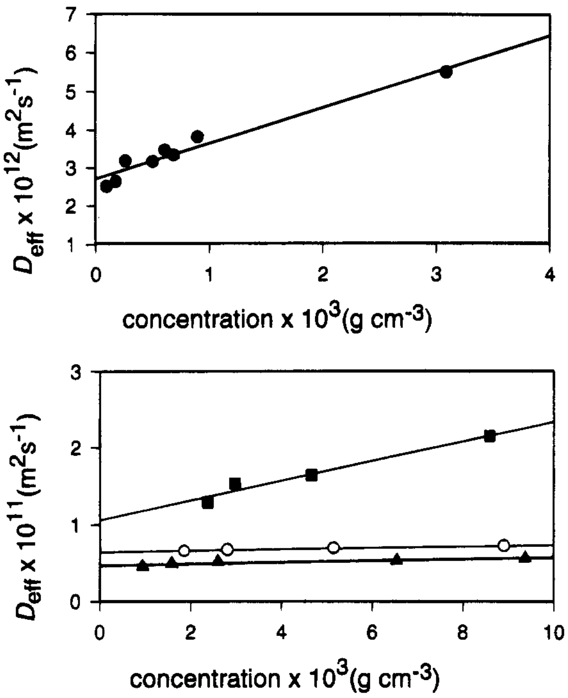

Figure 4. Plot of the effective diffusion coefficient (D_{eff}/m^2 s^{-1}) versus concentration (C/g cm^{-3}) for different micellar solutions: (●) 1400-*b*-310 prepared by dialysis against distilled water; (■) 500-*b*-60; (○) 1400-*b*-310 prepared by dialysis deionized water; (▲) 1140-*b*-170.

We define the diffusion coefficient thus obtained as the effective diffusion coefficient, D_{eff}. It is clear that the value of D_{eff} obtained depended on the concentration of the solution. In particular, as the concentration of the solution was increased, the value of D_{eff} increased. This is shown more clearly in Figure 4, where a plot of D_{eff} versus polymer concentration (C/g cm^{-3}) is presented for different micellar systems. The data in Figure 4 clearly illustrate that, within the variation of D_{eff} (~±5%) and the error in C (±3%), there is a linear variation of D_{eff} with respect to concentration, in the concentration ranges studied. From theory, it can be shown that the mutual diffusion coefficient, D,[28] obtained at finite concentration, is characterized by the concentration coefficient, k_D, in the expansion:[29]

$$D = D_0(1 + k_D C + ...) \tag{6}$$

where D_0 is the mutual diffusion coefficient, obtained by extrapolating vales of D obtained at finite concentrations to finite dilution.

For dilute solutions, k_D contains thermodynamic and hydrodynamic (frictional) components:[29]

$$k_D = 2A_2M_w - K_f - \nu \tag{7}$$

where A_2 is the second virial coefficient, M_w is the weight-average molecular weight of the diffusing species, K_f is the frictional coefficient, and ν is the partial specific volume of the polymer in the solvent.

One quantity that is readily obtained from the plots of D_{eff} versus C is the mutual diffusion coefficient at infinite dilution, D_0. Furthermore, by substituting the experimentally determined values of D_0 into the Stokes–Einstein equation, it is possible to obtain the hydrodynamic radius of the micelle, r_h:

$$r_h = kT/6\pi\eta D_0 \tag{8}$$

where k is the Boltzmann constant (J K^{-1}), T is the absolute temperature (K), and η is the viscosity of the solvent (N m^{-2} s). Values of the hydrodynamic radii of different samples are listed in Table 2. The notation used, i.e., $[(1/r_h)_z]^{-1}$, illustrates that the average radius obtained by DLS is the inverse reciprocal z-average hydrodynamic radius.

3.4.3. Coronal Thickness and the Degree of Extension of Coronal Chains.

One of the major reasons for accumulating these data was to gain an estimate of the thickness of the coronal layer in micelles of this type. From these data, it is also possible to calculate the degree of extension of the poly(acrylic acid) chains in the corona, by comparing the thickness of the corona with the fully extended contour length of the poly(acrylic acid) chains. The thickness of the corona may be obtained by subtracting the z-average core radius $[(r_{core})_z]$ from the inverse reciprocal z-average hydrodynamic radius. The percentage extension can be calculated from eq 9, where a is the length of one fully

$$\% \text{ extension} = \frac{100\{[(1/r_h)_z]^{-1} - (r_{core})_z\}}{aN_A} \tag{9}$$

extended acrylic acid repeat unit (assumed to be 0.25 nm). Values of the coronal thickness, $[(1/r_h)_z]^{-1} - (r_{core})_z]$, and the % extension of poly(acrylic acid) chains are presented in Table 2.

Before discussing these results, it is necessary to consider the various factors which influence the magnitude of the coronal thickness and % extension values. As already mentioned, the average radius obtained by DLS is the inverse reciprocal z-average hydrodynamic radius, which, in the case of polydisperse samples, is larger than the weight- and number-average hydrodynamic radius. Whenever possible, the same type of averages should be compared. It is possible to calculate the z-average core radius, $(r_{core})_z$, from the distribution of measured core radii; however, since the distribution of core radii is relatively narrow, the calculated z-average radius is not very different than the number-average radius. Unfortunately, in the present experiments, we did not have access to data analysis software from which we could calculate the number-average hydrodynamic radius. As a consequence, the intensity (I)-weighted values of the coronal thickness and % extension quoted in Table 2 represent the upper limit to the possible values.

Other factors which influence the magnitude of the values in Table 2 are the variation and errors in the different parameters. Obviously, $[(1/r_h)_z]^{-1}$, $(r_{core})_z$, and N_A are averages which are subject to experimental uncertainty: the uncertainty in $[(1/r_h)_z]^{-1}$ is approximately equal to the variation in D_{eff} (~±5%), the error involved in measuring r_{core} is around ±1 nm (5–8%), and the error in N_A is around ±5%. It must be recognized, therefore, that a combination of all these errors leads to a rather large error in the value of the coronal thickness and the value of the % extension.

Having recognized the factors which influence the values in Table 2, it is now possible to state, with confidence, that the poly(acrylic acid) chains in the coronas of micelles formed at high pH and at low ionic strength have an extremely extended conformation.

3.5. Factors Affecting the Stretching of Coronal Chains.

In this section, we discuss the various factors which are known to influence the conformation of chains in the coronal layer of micelles. The conformation of chains in the corona of a micelle is known to be affected by a variety of parameters, including the curvature of the micelle core to which the chains are attached, the concentration of chains in the corona, the chemical nature of the coronal chains, the quality of the solvent for the coronal chains, and the macroscopic concentration of micelles.[4,11–17,48–60] How each of these variables may contribute to the stretching of the coronal chains observed in the present experiments is discussed below. As part of this discussion, we present results obtained on the present micellar systems, as well as a comparison of our results with results available for other micellar systems.

3.5.1. Stretching of Coronal Chains: A Selective Summary of the Available Literature. We begin our discussion by briefly overviewing some of the literature relevant to this study. While there have been quite a few studies of the dimensions of micelle cores,[20,21,30–37] direct determination of the coronal thickness in micellar aggregates is more difficult,[21,33,34,38–40] since it involves the measurement of both the core and micelle radii. One study of this type was performed by McConnel et al. on polystyrene-*b*-polyisoprene micelles in decane, using a combination of small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS) and DLS experiments.[21] By subtracting core radii, obtained using SAXS and SANS, from hydrodynamic radii, they were able to obtain coronal thicknesses for a range of samples. Their experiments showed that the conformation of chains in the coronal layer of micelles is perturbed in comparison to the free homopolymer; i.e., the coronal thickness is larger than the root-mean-squared end-to-end distance of equivalent free homopolymer chains of the same molecular weight in the same solvent. This result has also been obtained by other authors.[33,34,38,39] For the polystyrene-*b*-polyisoprene micelles in decane studied by McConnell et al., the chains in the micelle coronas were much less extended than those in the present study, with % extension values in the range 16%–35%, depending on the sample.[21]

The results obtained by McConnell et al. were consistent with results obtained by Cogan et al. in an earlier study of micelles formed from polystyrene-*b*-poly(oxyethylene) block copolymers in cyclohexane.[39] In the study of Cogan et al., the degree of stretching of the coronal chains in the micelles was found to depend on the relative balance between the composition of the copolymer, the size of the micelle core, the aggregation number, and the length of the coronal chains. For example, micelles formed from copolymers consisting of relatively short core-forming blocks and relatively long corona-forming blocks formed micelles which resembled star polymers; e.g., their scattering profiles were consistent with a concave coronal density profile.[16] Micelles formed from copolymers consisting of relatively long core-forming blocks and relatively short corona-forming blocks had a very different structure which could not be described by the star model. For those systems, it was found that as a consequence of the higher concentration of chains in the corona, the coronal chains had a highly extended conformation. Using experimental values of r_h and N_A obtained by Cogan et al. for this sample, and an estimated value of r_{core}, we calculated that the coronal chains in micelles of a poly(oxyethylene)-*b*-polystyrene block copolymer (65-*b*-80) were approximately 70% extended.

In other studies of the micelle structure, a structural parameter of the micelle was measured, e.g., r_h, and a structural model was invoked to calculate the unknown parameter, e.g., r_{core}.[18,31,33,41,42] Two examples of this approach are outlined below. In a recent SANS study of block copolymers micelles formed from triblock copolymers of poly(oxyethylene)-*b*-poly(oxypropylene)-*b*-poly(oxyethylene) micelles in water, Pospíšil et al. used the spherical core/shell micelle model to estimate micelle structural parameters.[42] From SANS measurements, the authors were able to show that the micelle core was swollen. One controversial result that was obtained was that the shell thickness was 20% bigger than the fully extended length of the poly(oxyethylene) chain. The authors attributed this result to micelle and compositional polydispersity or to the existence of a poorly defined core–shell interface.

In another paper, Qin et al. studied micelles formed from polystyrene-*b*-poly(methacrylic acid) copolymers in a mixed solvent of 80 vol % dioxane and 20 vol % water by a wide range of experimental techniques.[18] The micelles were found to behave thermodynamically and hydrodynamically as impermeable spheres. By modeling their micelles as hard spheres, they were able to calculate the micelle core radii for two different cases: a completely unswollen core and a core with extensive swelling. Furthermore, from the measured values of r_h and the calculated values of r_{core}, they were able to estimate the degree of extension of chains in the corona. The results depnded on whether it was assumed that the core was swollen or unswollen and varied for different samples. For a dry core, the % extension varied between 39% and 94%; for the more realistic case of a swollen core, the authors calculated that the % extension varied between 32% and 58%.

3.5.2. Surface (Interface) Area per Coronal Chain (A_C/nm^2). The conformation of chains adsorbed at, or tethered to, a surface is known to be influenced by the density of chains at the surface. The influence of surface density on the conformation of chains has received both theoretical[43,44] and experimental[45] attention in recent years. The density of attached chains is considered low if the attached chains do not overlap. We can obtain an estimate of the surface (interface) area per coronal chain (A_C/nm^2) from the equation

$$A_C = 4\pi(r_{core})^2/N_{agg} \tag{10}$$

A complete list of values of A_C is given in Table 1.

It has been argued that the surface area per coronal chain may be an important factor among those controlling aggregation number and the structure of the micelles.[18,19] In particular, it has been suggested that in micelle formation, the interface energy between the core-forming block and solvent and the osmotic force acting on the corona-forming chains balance in a way so that a constant interface area per chain is maintained. This is clearly not observed in the present experiments. Our results suggest that the value of A_C increases as the total length of the block copolymer is increased. However, it must be remembered that the aggregation numbers contained in Table 1 were calculated from the micelle core radius. As such, we prefer to await results obtained from static light scattering, which will give a direct measure of N_{agg}, before discussing this observation further.

Using the approximate values of A_C contained in Table 1, it is possible to gain an *estimate* of the surface density of coronal chains for different micellar systems.

Using the approach of Hadziioannou et al.,[45] the dimensionless surface density for a planar surface, σ, is defined as $\sigma = A_C^{-1}a^2$, where a^2 is the area taken up by a single monomer segment (0.25^2 nm^2). For a polymer in a good solvent, the condition for low surface density is $\sigma < N_A^{-6/5}$. As σ becomes greater than $N_A^{-6/5}$, chains adopt conformations extended in a direction perpendicular from the surface, in order to accommodate the higher lateral packing of anchored chains at the surface. For the samples studied in the present experiments, the calculated value of the ratio $\sigma/N_A^{-6/5}$ was greater than unity only in three cases, i.e., for micelles formed from the polymers 740-*b*-180, 1140-*b*-170, and 1400-*b*-310, all micelles with relatively small core radii and relatively long coronal chains. However, the density of coronal chains obtained for all the micelles in the present study were low in comparison to micelles formed by other block copolymers, for example, the ratio $\sigma/N_A^{-6/5}$ lies in the range 9–200 for the starlike micelles studied by Nguyen et al.[20] The high degree of extension observed in the present experiments cannot, therefore, be attributed to a high density of coronal chains at the micelle core. If anything, the surface density of coronal chains is rather low.

3.5.3. Curvature of the Micellar Surface. Another factor which influences the thickness of the coronal layer is the degree of curvature of the surface to which the coronal chains are attached. Dan and Tirrell[46] have treated this effect theoretically using a self-consistent field model to compute the segment density profiles, layer thicknesses, and the distribution of chain ends, for chains tethered by one end to a curved impenetrable surface. The influence of geometry of the surface, the length of the tethered chain, the surface density of chains, and the radius of curvature can be seen in the relation for the average brush height, $\langle L\rangle$:

$$\langle L\rangle \sim aN_A^{3/(3+D)}\sigma^{1/(3+D)}(R/a)^{D/(3+D)} \qquad (11)$$

where R is the interface radius (r_{core} for spherical micelles). D is related to the dimensionality of the curvature for a particular geometry and is equal to 0 in planar geometry, 1 for cylinders, and 2 for spheres. From this relation, it can be seen that a spherical micelle with a large core (large value of R/a) will have a larger average brush height than a spherical micelle with a small core (small value of R/a). In the limit of very large spherical micelles, the curvature of the core becomes small and the average brush height approaches that of the planar brush attached to a flat surface. From experimentally determined values of r_{core} it is possible to calculate an approximate value of the ratio (R/a) for different micellar systems. These calculations show that as a consequence of their relatively large core radii, the micelles in the present study have (R/a) values in the range 48–84, comparable to the calculated range of values of (R/a) obtained by McConnell et al.[21] for polystyrene-*b*-polyisoprene micelles in decane (30–82), but bigger than the range of (R/a) values obtained by Nguyen et al.[20] for polystyrene-*b*-poly(cesium acrylate) and polystyrene-*b*-poly(4-vinylpyridinium–methyl iodide) reverse micelles in toluene (7–24).

3.5.4. Chemical Nature of the Coronal Chains and the Quality of the Solvent for the Coronal Chains. While the surface density of coronal chains and the core curvature undoubtedly affect the conformation of chains in the coronas of micelles, it seems that, considering the high degree of extension observed in the present experiments, the most important factors have not been addressed, i.e., the chemical nature of the coronal chains and the quality of the solvent for the coronal chains. It has already been noted that in the present experiments, as a consequence of the way the micelle systems were prepared, different micellar solutions had different pHs (see Table 2). This aspect of the study is rather unfortunate, since the pH of the solution determines (and gives an indication of) the degree of ionization, α, of the poly(acrylic acid) chains. It is, in principle, possible to calculate the degree of ionization of the coronal chains from data on the acid–base behavior of poly(acrylic acid) in water.[9,10] However, the acid–base behavior of poly(acrylic acid) in the corona of a micelle is undoubtedly different from the behavior of the free homopolymer in solution;[47] an unambiguous estimate of α is therefore difficult. We can, however, make the general statement that the chains in the coronas of the micellar samples prepared by dialysis in distilled water are neutralized by counterions introduced during the dialysis and, as a result, have an appreciable degree of polyelectrolyte character.

The principal difference between grafted neutral polymer and grafted polyelectrolyte layers is related to the difference in the nature of the interpolymer interactions in the two system, i.e., short-range excluded volume type interactions in the case of neutral polymers and long-range electrostatic interactions in the case of ionic polymers. As a consequence of long-range electrostatic repulsion, the chains in an adsorbed or tethered polyelectrolyte adopt a highly extended conformation at relatively low surface densities.[48]

3.5.5. Comparison of Experimental Results to Other Theoretical and Experimental Studies of Polyelectrolyte Colloids. 3.5.5.1. Theoretical Studies. There are a number of theoretical studies of polyelectrolytes adsorbed, or attached, to a planar surface[48–55] or attached to the surface of a spherical colloid particle.[48,53,55–61] In the case of a polyelectrolyte grafted to a flat surface with no added electrolyte, Pincus found that the brush thickness, L, was determined by a balance between the swelling effect of the counterions trying to increase their entropy by mixing and the chain elasticity.[48] He also found for this case that the chains were highly stretched for low degrees of ionization and that the brush thickness was independent of the grafting density. For the case of polyelectrolyte chains attached to a spherical colloidal particle, many theoretical treatments predict that the polymer chains will be strongly stretched radially. Using a self-consistent mean-field Monte Carlo approach to probe the conformational equilibria of chains in the corona of spherical polyelectrolyte micelles, Ronis predicted that the chains in the coronal layer do not adopt a single conformation.[57] Rather, the coronal layer is composed of three subregions: a rigid rodlike region near the core, followed by a flexible-rod region and a continuum region at the end of the chain. He also showed that the extent of rodlike or coil-like conformational behavior depended on the length of the chain, the core size, the aggregation number, and the screening length.

The high degrees of extension of coronal chains which we observed experimentally in samples prepared by dialysis against distilled water (which have a high degree of neutralization) are therefore reasonable. In water, the intramolecular repulsion between chains in the corona causes the chains to adopt a highly extended conformation. Using the terminology of Pincus,[48] the coronal chains resemble porcupine quills.

Another feature of some of the theoretical models is that the conformation of the polymer chains attached to spherical colloidal particles is strongly affected by the presence of added electrolyte and by changes in the degree of ionization of the polyelectrolyte chains.[48,52,53,55,57,58] These studies are allied with a substantial body of literature on the conformation of polyelectrolytes,[27] which shows that, in the presence of salt, the range of electrostatic repulsion is reduced and the chains adopt a more random coil conformation. In a recent paper Ronis also considered the effect of micelle–micelle interactions at finite colloid concentrations.[58] For the concentrations and surface coverage studied, he found that the conformation of chains was mainly affected by intra-aggregate interactions; inter-aggregate interactions did not perturb the conformation appreciably. It is worthwhile to note that all hydrodynamic radii were calculated from the extrapolated value of the diffusion coefficient at infinite dilution. At the limit of infinite dilution, inter-aggregate interactions should not influence the size of the micelle.

The data presented in Table 2 provide a test of the theoretical studies outlined above. For example, by studying the variation of the hydrodynamic radius with respect to salt concentration, or degree of neutralization, it should be possible to investigate the balance of physical forces which influence the conformation of polyelectrolyte chains attached to a colloidal surface. We have recently compared our experimental results to the theoretical model developed by Ronis.[57,58] Preliminary results suggest that theoretical predictions of the degree of chain extension are in agreement with experiment. Further work will involve probing the conformation of the chains in the coronas of a wider range of samples, spanning a broader range of copolymer compositions. It should be noted that in water, or in aqueous salt solutions, the micelles have a frozen structure and that changes to the ionic strength or degree of neutralization should not influence parameters which depend on the dimensions of the core; therefore, r_{core} and N_{agg} will not change.

As part of a preliminary study of the effect of the salt concentration and degree of neutralization of the coronal chains on the degree of extension of coronal chains, we present results obtained on micelles formed from the copolymer 1400-*b*-310. This copolymer was chosen since it contains micelles which have the longest coronal chains. The micelles formed from this copolymer also have the largest hydrodynamic radius of all the different samples studied here; any effects due to the dimensions of the coronal chains should be most easily measured in this sample. When the micelle sample was prepared in deionized water, the resulting micellar solution had a pH of ~4.5. This indicates that the degree of ionization of the polymer chains was low. For this sample the micelle hydrodynamic radius was 38 nm, which is 2 times smaller than that at pH 7. The corresponding value for the % extension of coronal chains was 25%, comparable to the values obtained by McConnell et al. for polystyrene-*b*-polyisoprene micelles in decane.[21] The influence of the degree of neutralization is thus clear: introducing ionic charges to the polymer chain results in an appreciable expansion of the coronal chains. The resemblance of micelles formed from copolymers with essentially non-ionized poly(acrylic acid) to neutral polymers is also apparent.

Another way of influencing the conformation of polyelectrolyte chains is to add an inert electrolyte to the solution. Preliminary data for the sample 1400-*b*-310 in 1 M NaCl also show that the hydrodynamic radius of the micelle decreases in the presence of an electrolyte. One interesting aspect of this study is that the hydrodynamic radius in the presence of salt (48 nm) was smaller than the hydrodynamic radius in the absence of salt (90 nm), but larger than the hydrodynamic radius of the sample at pH 4.5 (38 nm) (it should be noted that the hydrodynamic radius of the sample with added salt was obtained by extrapolation through only three data points; this is because on dilution of this sample flocculation occurred: see below). This result suggests that ionized coronal chains, in the presence of salt, are more stretched than coronal chains with a low degree of ionization. This effect has been predicted theoretically by Pincus,[48] who suggested that the addition of electrolyte (Debye screening) reduces the counterion osmotic pressure, which stretches the polymer chains.

The effect of the addition of salt on the dissociation equilibrium of the carboxylic acid groups and the neutralized carboxylic acid groups is also of importance. For example, it is well-known that the addition of a salt to a polyelectrolyte solution leads to a decreases in the pK_a of the polyelectrolyte.[10] This effect, reflected in the lower pH of the sample in the presence of salt (see Table 2), illustrates that the activity of the proton is increased in the presence of NaCl. The addition of salt to a solution of an ionized polyelectrolyte micelle thus leads to a number of component effects: Debye screening and a change in the acid–base equilibria. This result also illustrates that in order to study the effect of the addition of salt on the degree of stretching of the coronal chains, it is necessary to ensure that the ionic strength and degree of ionization of the initial polyelectrolyte solution are known.

Another interesting observation for the sample in the presence of salt was that flocculation occurred on dilution of this sample with 1 M NaCl. It was possible to redisperse the flocs by placing the sample in a sonic bath, but the flocculated structure was formed again when the sample was left to stand for a few hours. After an extended period of standing (10 days), the cloudy solution eventually settled to form a two-phase system. It was not possible to form a one-phase system by increasing the pH of the continuous medium. We consider the loss of colloidal stability observed for this sample to be a consequence of the relatively low density of coronal chains at the surface. This effect, noted in our previous study of micelles formed from polystyrene-*b*-poly(4-vinylpyridinium–methyl iodide) block copolymers,[5] has also been predicted by theory.[48] The critical dimension in determining the degree of screening is the density of chains at the surface, i.e. the grafting density: the lower the grafting density, the more sensitive the colloid is to added electrolyte.

3.5.5.2. Experimental Studies. While the direct determination of the thickness of the coronal layer in spherical polyelectrolyte micelles is certainly one novel aspect of this work, the observation that the structure of block copolymer micelles composed of a hydrophobic core and ionogenic corona depends on the pH and the ionic strength is not new. The fact was recognized early in the development of the field,[62,63] but was not studied systematically. More recently, Tuzar, Munk, and coworkers[26,47,64] have studied micelles formed from polystyrene-*b*-poly(methacrylic acid) block copolymers by a variety of experimental techniques, including DLS. In the first of these studies, they found that the apparent hydrodynamic diameter of the micelles increased as the degree of neutralization increased.[26] They attributed this result to the expansion of the poly(methacrylic acid) blocks in the shell of the micelle. Core dimensions were not determined in this study, but from a knowledge of the block lengths and the aggregation number we estimate that the % extension of coronal chains at a degree of neutralization $\alpha = 1$ was ~45%–70%, depending on the concentration. For ionized micelles at concentrations $\geq 5 \times 10^{-3}$ g cm^{-3}, DLS experiments were affected by order formation in solution. The distribution of apparent hydrodynamic radii became broad and the autocorrelation curve became nonexponential.

In another study, the hydrodynamic radius of micelles was measured as a function of pH for polystyrene-*b*-poly(methacrylic acid) block copolymer micelles in various buffer solutions.[64] Again, the authors found that as the pH of the solution was increased, the hydrodynamic radius increased. The coronal dimensions were not determined in this study. However, we estimate that the degree of expansion of the coronal chains observed in these experiments was smaller than that observed in our experiments. For example, as the pH was changed from 5 to 7.8, using buffers, the % extension increased from ~25% to ~32% for one sample, and from ~25% to ~38% for another sample. We consider the lower values of the % extension observed in these studies to be a consequence of the fact that buffer solutions contain an appreciable concentration of salt. It is thus difficult to separate the effect of an increase in pH on the extension of coronal chains from the effect of an increase in the ionic strength. The different chemical nature of the coronal chains will also be of influence. In particular, it is known that poly(methacrylic acid) has very different acid–base and solubility behavior than poly(acrylic acid).[10]

4.0. Summary

In this study, we have been able to gain valuable information about the structure of polystyrene-*b*-poly(acrylic acid) micelles in water. Because of the versatility of the synthetic method, it was possible to synthesize a wide range of different copolymer samples and study the effect of the length of the insoluble block (N_B) and the length of the soluble block (N_A) on the structure of the micelles. One of the important aspects of this work is that the micelle core radius, r_{core}, appears to depend not only on the length of the insoluble polystyrene block but also on the length of the soluble poly(acrylic acid) block. Although an extensive comparison of our experimental data with theory was not attempted, our experimental results suggest that the length of the soluble block is an important parameter among those determining the structure of micellar associates. It is worthwhile to note that the inverse dependence of the core radius on the coronal block length has been observed previously[35] and that the value of the exponent, γ, describing this dependence is similar to that predicted by some theories.[14]

From values of the core radius, r_{core}, and the hydrodynamic radius, r_h, it was possible to obtain an estimate of the thickness of the coronal layer of the micelles and the degree of extension of the coronal chains. It was found that the poly(acrylic acid) chains were highly extended in samples at a pH of ~7. A brief overview of some of the current literature on coronal dimensions in micelles was presented, as was a discussion of the various parameters which are known to influence the dimension of chains in the coronas of micelles. Results obtained here were compared with various data from other experimental studies of micelle structure, and a discussion of results in relation to a number of theoretical studies was presented. We consider the high degree of extension of coronal chains observed in the present experiments to be due to the charged nature of the poly(acrylic acid) chains, the low degree of curvature of the surface to which the chains are attached, and the relatively low macroscopic concentration of micelles in the DLS experiments. In many ways the coronal chains resemble the polyelectrolyte brushes which currently excite much interest.[55]

Data of these type provide a test of many of the theoretical models available in the literature. We have recently compared our results with a theoretical model developed by Ronis,[57,58] which uses a self-consistent mean-field Monte Carlo approach to probe the conformational equilibria of chains in the coronal layer of spherical polyelectrolyte micelles. Preliminary results suggest that theoretical predictions of the chain conformation are in agreement with experiment. Future work will involve probing the conformation of the chains in coronas of a wider range of samples, spanning a broader range of copolymer compositions. The influence of the degree of ionization and the pH of the micellar solution on the conformation of the coronal chains will also be investigated. These studies are currently underway in our laboratory and results will be reported in the near future.

Acknowledgment. We would like to acknowledge the National Sciences and Engineering Research Council of Canada (NSERC) for funding this work. We would like to thank Dr. T. G. M. van de Ven, director of the Pulp and Paper Research Institute of Canada, for permission to use the center's DLS equipment. The various contributions of Matthew Moffitt during the writing of this paper are also gratefully acknowledged.

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MA950138F