Micellization Behavior of Poly(butadiene-*b*-sodium methacrylate) Copolymers in Dilute Aqueous Media

Stergios Pispas and Nikos Hadjichristidis*

Department of Chemistry, University of Athens, Panepistimiopolis Zografou, 157 71 Athens, Greece

Received May 14, 2003; Revised Manuscript Received September 15, 2003

ABSTRACT: The aggregation behavior in dilute aqueous solutions of a series of poly(butadiene-*b*-sodium methacrylate) copolymers, produced from the corresponding anionically synthesized poly(butadiene-*b*-*tert*-butyl methacrylate) copolymers, was investigated by static and dynamic light scattering. Micellar characteristics, including aggregation number, size, and polydispersity, were found to depend on the molecular weight and the composition of the copolymers. In addition to spherical micelles, supramicellar aggregates were also detected in the case of very short corona blocks. Measurements at different temperatures indicated a decrease in the size of the spherical micelles by increasing temperature, probably due to worsening of the thermodynamic quality of water toward the micellar corona. The presence of a small amount of NaCl in the solutions affects the structural characteristics of the aggregates, as indicated by an increase in the aggregation number and size of the micelles. However, small structural changes where observed as a function of salt concentration in the region 0.1 to 1.0 M NaCl.

Introduction

Block copolymers in selective solvents form micelles, in a manner analogous to low molecular weight surfactants. The phenomenon was identified several decades ago but still constitutes an area of intensive academic and industrial research.[1−4] The majority of properties and applications of the micellar systems stem from their core−shell structure. Considerable attention has been devoted to understanding the relationships between molecular characteristics of the copolymer (molecular weight, composition, and molecular architecture) and physicochemical parameters (concentration, temperature, and solvent quality) to the final properties of the micelles (aggregation number, size, shape, stability, etc.), mainly in organic solvents.[1−17] The structure−properties relationships are useful in finding new ways of altering micellar properties and functions and in designing application-oriented systems.

Lately, amphiphilic block copolymers, i.e., block copolymers, consisting of a hydrophobic and a hydrophilic block have attracted the interest of scientists because of their solubility in water and their potential applications.[18,19] For example, amphiphilic block copolymers can be used for the controlled release of pharmaceutical substances into living organisms (smart carriers) as well as in environmental purification technologies for the encapsulation and removal of toxic hydrophobic substances from contaminated waters.[3,18] Block copolymers containing corona-forming blocks of anionic, cationic, or neutral type have been investigated so far with respect to their ability to form a variety of aggregates in water.[2,3,14,18−39] A plethora of aggregate morphologies have been identified in aqueous solutions of block copolymers with (meth)acrylic-type water-soluble blocks.

In this paper we report on the aggregation behavior of a series of poly(butadiene-*b*-sodium methacrylate) diblock copolymers in dilute aqueous solutions. Static and dynamic light scattering are used as the tools for studying the properties of the aggregates formed under different experimental conditions (concentration of the copolymer, temperature, and concentration of salt). The primary goal is to understand the fundamental principles governing the self-assembly of this type of amphiphilic block copolymer in solution and finding ways of controlling it at will. The low T_g (∼−90 °C) of the highly hydrophobic polybutadiene (PB) block makes these copolymers directly soluble in water in a wide range of compositions and molecular weights. In this way the use of mixed solvent for copolymer dissolution, which may complicate the aggregation process, is avoided. Furthermore, the low T_g of the PB chains ensures a higher mobility of the chains in the micellar core. Therefore, micellar systems closer to the equilibrium state are anticipated to be obtained. Additionally, the presence of double bonds in the core-forming block offers the possibility of stabilizing the resulting structures in solutions by cross-linking[40,41] or of changing the chemical nature of the core by postpolymerization reactions, producing core−shell-type nanoparticles and systems with different chemical natures and properties.

Experimental Section

Polymer Synthesis. The diblock copolymer precursors containing polybutadiene (PB) with high 1,4 microstructure and *tert*-butyl methacrylate blocks were synthesized for anionic polymerization high-vacuum techniques.[42] All monomers, solvents, and reagents were carefully purified to the standards required by anionic polymerization according to well-established techniques. Butadiene monomer was first polymerized in benzene using *sec*-BuLi as the initiator. After completion of the polymerization a sample was withdrawn for molecular characterization of the polybutadiene block. The active PBLi solution was transferred into ampules equipped with break-seals and sealed off from the reactor. The ampule containing the active PBLi solution was attached to a second polymerization reactor containing THF, in 2.5 times volume excess over the volume of PBLi solution in benzene. To this reactor were also attached ampules containing purified 1,1-diphenylethylene (DPE) in hexane (in 2−5 times molar excess over the living ends), LiCl in THF (5 times molar excess over the living ends), and purified *tert*-butyl methacrylate (tBMA) monomer. The reactor was immersed into a dry ice/2-propanol bath at −78 °C, and DPE, LiCl, and PBLi were introduced in that order under stirring, by breaking the appropriate break-seals. After about 15 min tBMA was introduced into the reactor by distillation from its ampule and allowed to polymerize for 4 h. The polymerization was finally terminated with degassed

10.1021/ma034627o CCC: $25.00

methanol. The copolymers were precipitated in methanol, containing 10−20 vol % distilled water, stabilized with 2,6-di-*tert*-butyl-*p*-cresol, after condensing the THF/benzene mixed solution in a rotor evaporator to about 30% of its initial volume. The samples were thoroughly dried in a vacuum oven for a period of 1 week or more, until constant weight. The samples were denoted as BBMA followed by a number representing the order of sample synthesis.

Synthesis of Poly(butadiene-*b*-sodium methacrylate) (NaBMA) Copolymers. The block copolymers containing a hydrophobic PB block and a hydrophilic poly(sodium methacrylate) polyelectrolyte block were synthesized by hydrolysis of the BBMA block copolymers and subsequent neutralization of the COOH groups with NaOH. Block copolymers were dissolved in distilled dioxane, to which a predetermined amount of HCl 6 N was added. A condenser was fitted to the round-bottom flask containing the polymer solution, and the temperature was raised at 85 °C, under a continuous stream of argon or N_2 flow to prevent side reactions on the PB block at the temperature of the reaction.[43,44] Preliminary experiments on PB homopolymers showed that the reaction scheme followed leaves the PB block unaffected, in terms of molecular weight, molecular weight distribution, and chemical constitution, as evidenced by size exclusion chromatography (SEC) and NMR spectroscopy. The reaction was allowed to proceed for 6 h. The solution was decanted in acetone, and the modified copolymers were washed repeatedly with acetone and dried in a vacuum oven.

The dry poly(butadiene-*b*-methacrylic acid) (BMA) block copolymers were dissolved in THF (about 2 wt % solution contained in a beaker with a Teflon stirring bar), and the stoichiometric amount of NaOH in ethanol was added dropwise through a volumetric buret under vigorous stirring. Stirring was continued for 1 h after completion of the NaOH addition to ensure complete neutralization of COOH groups. At the end of the neutralization process THF and ethanol were removed partially in a rotor evaporator, and the inhomogeneous solution was decanted in acetone. The solid copolymer was recovered and dried under vacuum. The use of solvents having a similar thermodynamic quality toward both blocks, i.e., good (dioxane, THF) or bad (acetone) solvents for both blocks during the functionalization and neutralizartion reactions, hopefully will lead to the formation of a nonselective, near-equilibrium, structure in the solid samples. The samples were denoted as NaBMA followed by the corresponding precursor number.

Characterization of Precursors and Derivatives. The BBMA precursors were characterized by a variety of methods. Size exclusion chromatography (SEC) was used for determination of molecular weight distribution and compositional homogeneity of the samples at 30 °C in THF at a flow rate of 1 mL/min, using a Waters system composed of a Waters 600 pump controller, a set of four Styragel columns (continuous porosity range 10^3-10^6 Å), a Waters 410 differential refractometer, and a Waters 996 photodiode array UV detector interfaced with a computer. The instrument was calibrated with nine linear polystyrene standards having molecular weights in the range 4000−900 000. Number-average molecular weights were determined by membrane osmometry (MO) in toluene, refluxed over CaH_2, and distilled prior to use, at 37 °C, using a Jupiter Instruments Co. model 231 membrane osmometer. Weight-average molecular weights were obtained by low-angle laser light scattering (LALLS) using a Chromatix KMX-6 low-angle laser light scattering photometer equipped with a 2 mW He−Ne laser operating at 633 nm. THF, refluxed over sodium metal and distilled just prior to use, was the solvent at 25 °C. The required specific refractive index increments, d*n*/d*c*, were determined with a Chromatix KMX-16 laser differential refractometer operating at the same wavelength and temperature and calibrated with aqueous NaCl solutions. The microstructure of the PB blocks and the average composition of the precursor copolymers were determined by ^{1}H NMR spectroscopy using a Varian 200 MHz instrument in $CDCl_3$ at 30 °C.

The extent of the postpolymerization reactions was determined by solid-state ^{13}C NMR using a Bruker MSL 400 spectrometer capable of high-power ^{1}H-decoupling and equipped with a magic angle spinning unit at 30 °C. The degree of conversion was checked through the appearance and disappearance of the characteristic peaks corresponding to the various chemical groups incorporated in the starting and the final materials. More details about the sample synthesis and molecular characterization are given elsewhere.[45] The molecular characterization results for the BBMA precursors and the NaBMA block polyelectrolytes are given in Tables 1 and 2, respectively.

Table 1. Molecular Characteristics of the Poly(butadiene-*b*-*tert*-butyl methacrylate) Precursors

sample	$M_w{}^a \times 10^{-4}$	$M_n{}^b \times 10^{-4}$	$M_{n,PB}{}^b \times 10^{-4}$	$M_w/M_n{}^c$	wt % PB^d
BBMA-6	0.92	0.85^e	0.32^c	1.07	38
BBMA-9	0.71	0.63^e	0.32^c	1.06	51
BBMA-3	3.36	3.08	1.14	1.09	37
BBMA-5	8.60	7.99	2.99	1.07	37

^{a} By LALLS in THF at 25 °C. ^{b} By membrane osmometry in toluene at 37 °C. ^{c} By SEC in THF at 30 °C. ^{d} By ^{1}H NMR in $CDCl_3$ at 30 °C. ^{e} By LALLS and SEC.

Table 2. Molecular Characteristics of the Poly(butadiene-*b*-sodium methacrylate) Copolymers

sample	$M_w{}^a \times 10^{-4}$	N_{PB}	N_{PNaMA}	wt % PB^a
NaBMA-6	0.72	59	37	44
NaBMA-9	0.56	59	22	57
NaBMA-3	2.62	211	137	44
NaBMA-5	6.79	554	352	44

^{a} Calculated from the molecular characteristics of the corresponding precursors (Table 1) assuming complete hydrolysis and neutralization of the carboxylic groups.

Preparation of Micellar Solutions. A Millipore Milli-Q 184 water purification system was used for purification of the water used for the preparation of the copolymer solutions. Stock solutions were prepared by dissolving a weighed amount of sample in the appropriate volume of purified water, filtered through 0.45 μm hydrophilic Teflon Millipore filters, with occasional stirring. Direct dissolution of the copolymers in water is possible mainly due to the low T_g of the PB block, as already mentioned in the Introduction. For the samples with the higher molecular weight and higher PB content, the stock solutions were heated at 60 °C overnight to facilitate complete dissolution of the samples and removal of possible memory effects. Stock solutions had the characteristic bluish tint related to the presence of micelles. These solutions were subsequently dialyzed against Milli-Q water for at least 4 days, using Spectra/Por 7 dialysis membranes with a nominal molecular weight cutoff of 3500, from Spectrum Laboratories Inc. The concentration of the solutions before and after dialysis was checked gravimetrically by evaporating a known volume of the solution. Less than 5% change in concentration was determined after dialysis, and the concentration of the solution was corrected accordingly. Solutions of lower concentration were obtained by subsequent dilution of the stock solutions.

NaCl (analytical grade from Merck) was dried at 120 °C before use. Block copolymers were dissolved in the salt containing solutions followed by dialysis. In this case changes in the polymer concentration were determined by measuring the light scattering intensity at 90° before and after dialysis. A decrease in the solubility of the samples by increasing salt concentration was observed. The effect was more pronounced for the higher molecular weight samples. Complete dissolution was accomplished by increasing the heating period. Especially, the highest molecular weight sample was insoluble in salt solutions. Before light scattering measurements all solutions were filtered through 0.45 μm hydrophilic Teflon filters (Millex-LCR) obtained from Millipore. No problems were encountered during filtration. However, sample concentration before and after filtration was checked in the case of water solutions gravimetrically. No changes in the quantity of the solubilized sample were noticed.

Micellization Studies. Initial light scattering measurements were performed at 25 °C with the Chromatix KMX-6 low-angle laser light scattering photometer described before. Apparent weight-average molecular weights, M_w, and second virial coefficients, A_2, were obtained from the concentration dependence of the reduced scattering intensity. Multiangle light scattering measurements were conducted with a series 4700 Malvern system composed of a PCS5101 goniometer with a PCS7 stepper motor controller, a Cyonics variable power Ar^+ laser, operating at 488 nm and with 10 mW power, a PCS8 temperature control unit, and a RR98 pump/filtering unit. Apparent mean-square radii of gyration, R_g, were determined from the initial slope of the angular dependence of the reduced scattering intensity measured at angles between 30° and 135°. Toluene, dried over CaH_2 and fractionally distilled, was used as a calibration standard. The following general equation was used in this case:

$$Kc/\Delta R_\theta = 1/M_w\{1 + [(16\pi^2 n_0^{\,2})/(3\lambda_0^{\,2})]\langle R_g^{\,2}\rangle \sin^2(\theta/2)\} + 2A_2c + \ldots \quad (1)$$

where $K = (2\pi n_0)^2(\mathrm{d}n/\mathrm{d}c)^2(N_A\lambda_0^4)^{-1}$, c is the polymer concentration, ΔR_θ is the excess Rayleigh ratio, θ is the scattering angle, n_0 is the solvent refractive index, λ_0 is the wavelength of light in a vacuum, dn/dc is the specific refractive index increment, and N_A is the Avogadro number. The required specific refractive indices, dn/dc, were obtained at 633 nm by a Chromatix KMX-16 laser differential refractometer and at 488 nm by an Optilab DSP (Wyatt Technology) interferometric refractometer, both calibrated with NaCl standard aqueous solutions, after dialysis against water and NaCl solutions. The weight-average molecular weight of copolymers determined by light scattering is an apparent quantity.[1,2] However, it is close to the true one when the molecular weight and compositional polydispersity of the copolymer are low (as is the case with the block copolymers in this study, which were prepared by anionic polymerization), and the dn/dc values of both blocks are high. The latter criterion is also met for the samples under investigation (dn/dc for NaPMMA in water equals 0.260 and $n_{PB} = 1.52$, $n_{water} = 1.33$ which ensures a high dn/dc value for the PB block, which is insoluble in water, and the absolute value of dn/dc cannot be measured directly); thus, we feel that the apparent M_w's determined are close to the true ones.

Dynamic light scattering experiments were carried out, at 25 °C, on the same Malvern system operating in the dynamic mode. A 192-channel correlator was used for accumulation of the data. Correlation functions were analyzed by the cumulant method, and the Contin software was provided by the manufacturer. Correlation functions were collected at angles between 45° and 135°. Apparent diffusion coefficients at zero concentration, $D_{0,app}$, were obtained after extrapolation to zero angle using eq 2:

$$D_{app} = D_{0,app}(1 + k_D c) \quad (2)$$

where D_{app} is the diffusion coefficient measured at each concentration and k_D the coefficient at the concentration dependence of D_{app}. Apparent hydrodynamic radii, R_h, were determined by equation

$$R_h = k_B T/6\pi\eta_0 D_{0,app} \quad (3)$$

where k_B is the Boltzmann constant, T the absolute temperature, and η_0 the viscosity of the solvent. Apparent hydrodynamic radii at each concentration were calculated by aid of eq 3 using the value for the D_{app} for each concentration. Polydispersity values were obtained from the cumulant analysis of the correlation functions. Temperature scans were performed by the same Malvern system, in the temperature range between 25 and 55 °C, at 5 °C intervals and at an angle of 90°. Measurements at other angles gave similar results. A period of about 30 min was allowed between measurements at different temperatures. The scattering intensity and correlation functions were recorded simultaneously. R_h values were calculated taking into account the variation of water viscosity in the same temperature range. Heating and cooling cycles were performed. The intensity, R_h, and polydispersity values were reproducible between subsequent heating and cooling scans.

Table 3. Light Scattering Results for NaBMA Block Copolymer Micelles in Water at 25 °C

sample	$M_{w, app} \times 10^{-6}$	$A_2 \times 10^5$	N_w	R_g (nm)	R_h (nm)	k_D	R_g/R_h
NaBMA-6	2.12	8.6	294		18.4	102	
NaBMA-9	6.8	1.8	1214	$80._7$	18, 98[a]		
NaBMA-3	15.2	~0	580	$34._6$	51.9	65	0.67
NaBMA-5	44.3	~0	652	$53._3$	94.7	28	0.56

[a] Bimodal distribution of hydrodynamic radii.

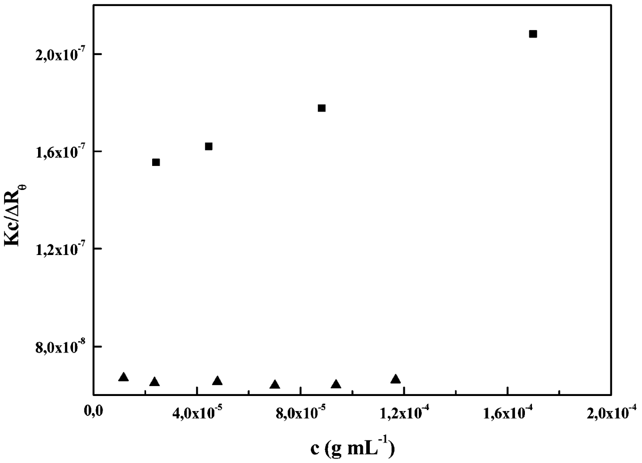

Figure 1. $Kc/\Delta R_\theta$ vs concentration plots for micelles of samples (■) NaBMA-9 and (▲) NaBMA-3 in water at 25 °C.

Results and Discussion

Micellization Studies in Water. The light scattering results for the NaBMA block copolymer micelles in water are summarized in Table 3. Static light scattering plots of $Kc/\Delta R_\theta$ vs concentration were linear in the concentration range studied (Figure 1). No indication of the presence of a cmc, as evidenced by an upturn of the plot in the low-concentration region of the graphs, was observed. Presumably, in this region, the equilibrium is shifted in favor of micelles. The molecular weights determined by linear extrapolation at zero concentration are much higher than the ones obtained for individual chains, thereby proving the presence of micelles in the solutions. The apparent second virial coefficients are very small (they decrease as the molecular weight of the copolymer increases) due to the unfavorable interactions between the hydrophobic core and water molecules. Some contributions from corona–corona and corona–solvent interactions to apparent A_2 are expected, but the main contribution is coming from the association of the core blocks due to incompatibility with the solvent. The increase in the molecular weight of the micelles also has the effect of decreasing the A_2 values. The aggregation number, N_w, calculated as the ratio of the micellar molecular weight to that of the isolated chain (unimer) increases as the molecular weight of the block copolymer increases (at constant composition) and as the PB content in the copolymer increases (at constant PB molecular weight, Table 3). An increase in the aggregation number, as the molecular weight and its weight fraction of the insoluble block increase, has been predicted theoretically and verified

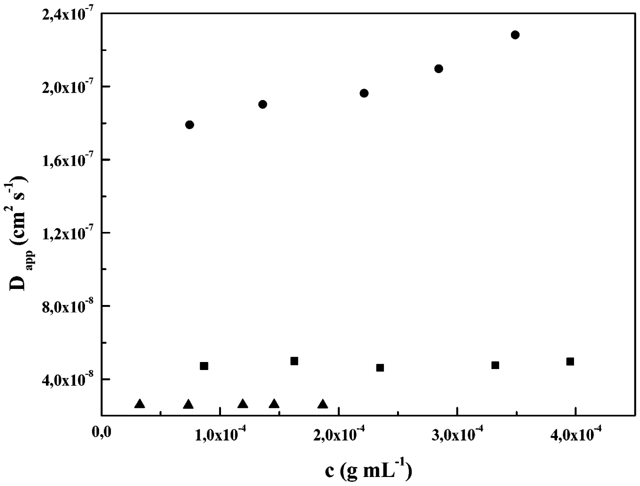

Figure 2. Diffusion coefficient vs concentration plots for micelles of samples (●) NaBMA-6, (■) NaBMA-3 and (▲) NaBMA-5 in water at 25 °C.

experimentally in other block copolymer micellar systems.[1−3] Absolute values of aggregation numbers are very high especially for the case of sample NaBMA-9, which has the higher PB content. Such large aggregation numbers, previously observed for other amphiphilic block copolymers with a hydrocarbon type insoluble block, can be attributed to the high hydrophobicity of the hydrocarbon blocks.[34,39]

Apparent hydrodynamic radii determined by DLS show a very weak concentration dependence (Figure 2). Contin analysis reveals the presence of only one type of diffusing species for aqueous solutions of samples NaBMA-6, NaBMA-3, and NaBMA-5. The average polydispersity of these systems, as evaluated through the ratio μ_2/Γ^2 by cumulants analysis, where μ_2 is the second moment in the cumulant expansion of the correlation function and Γ is its decay rate, is small ($\mu_2/\Gamma^2 < 0.1$). The presence of spherical micelles in the solutions of the aforementioned samples is dictated by their lower PB content and corroborated by the observation that the ratio R_g/R_h for the micelles, determined where possible, has values around 0.6. The R_g/R_h value for hard spheres is 0.775, but a nonuniform density profile has been shown to give even lower values.[10,46]

In the case of sample NaBMA-9, two populations were present at all concentrations studied. The small size population had an average R_h of 18 nm, and the larger aggregates had an R_h of 98 nm. The low R_h peak was considerably narrower than that corresponding to the larger component. The low R_h component must correspond to spherical micelles whereas that with the larger R_h may be attributed to micellar clusters or aggregates of shape other than spherical. Micellar clusters can be formed in this case as a result of the limited ability of the short PNaMAA coronas to shield the hydrophobic PB cores. As a consequence, clusters are formed through intermicellar core hydrophobic interactions. On the other hand, cylindrical micelles can be formed as a result of the increase in the aggregation number of the aggregate, which forces the PB chains to stretch in the core. Since this stretching is energetically unfavorable in spherical micelles, a shape transition, to cylindrical micelles, which will allow for a decrease in the elongation of the PB chains, is highly probable. The two scenarios cannot be distinguished by the experimental results available since both micellar clusters and cylindrical micelles are expected to have a higher polydispersity than spherical micelles.[10] TEM observations would be useful although in this case one should be very careful for the presence of artifacts produced by the sample preparation protocols.

Table 4. Structural Characteristics of the NaBMA Spherical Micelles in Water

sample	R_c (nm)	A_c (nm^2)	W_{corona} (nm)	L (nm)	av corona density (monomers/nm^3)
NaBMA-6	3.4	0.49	15	9.2	0.77
NaBMA-3	7.1	1.09	44.8	34.2	0.21
NaBMA-5	9.2	1.63	85.5	88	0.09

The structural characteristics of the spherical micelles are given in Table 4. The radius of the core, R_c, the area per junction point at the core−corona interface, A_c, and the width of the corona, W, have been calculated according to eqs 4, 5, and 6

$$R_c = (3M_{w,\,mic}\mathrm{wt}_{PB}/4\pi N_A d_{PB}\phi_{PB})^{1/3} \tag{4}$$

$$A_c = 4\pi R_c^{\,2}/N_w \tag{5}$$

$$W = R_h - R_c \tag{6}$$

It was assumed that the core is free from solvent ($\phi = 1$), a reasonable assumption since PB is highly hydrophobic. The density of PB was taken as $d = 0.89$ g cm^{-3}. Small differences on the value used for d_{PB}, as found in the literature, would not change the overall picture substantially. The density of the corona was calculated from the corresponding volume and the aggregation number and number of monomeric units per corona chain. It can be seen (Table 4) that R_c increases as the molecular weight of the PB block and the aggregation number increases. A_c is found to increase as the molecular weight of the corona chain increases. The width of the corona also increases with increasing the corona chain length. The length of the fully stretched corona chain, L, calculated from the number of monomers per chains and using a value of 0.25 nm as an average length per monomeric unit, is also given for comparison. It can be concluded that corona chains are highly stretched due to electrostatic repulsions stemming from their polyelectrolyte nature. In two cases W is larger than L. This may be attributed to the finite polydispersity of the micelles.[26] However, extension of the polyelectrolyte corona chains decreases as N_w increases (i.e., as R_c and A_c increases) since more space is available per chain. As a result of the high extension of the polyelectrolyte corona chains the average corona density is very low (Table 4). Of course, someone expects some variation (decrease) of the monomer density in the corona as the distance from the core increases, as it was inferred from recent experimental results.[21] Similar observations concerning the structural characteristics of micelles with polyelectrolyte coronas have been reported in the case of poly(styrene-b-sodium acrylate) micelles in water.[26,27] It seems that despite the differences in the chemical nature of the blocks, the T_g's of the cores, and the preparation protocol, the general behavior is similar.

Influence of Temperature. The effect of temperature on the structural characteristics of the NaBMA micelles in solution was also investigated. Figure 3, where the results from light scattering measurements

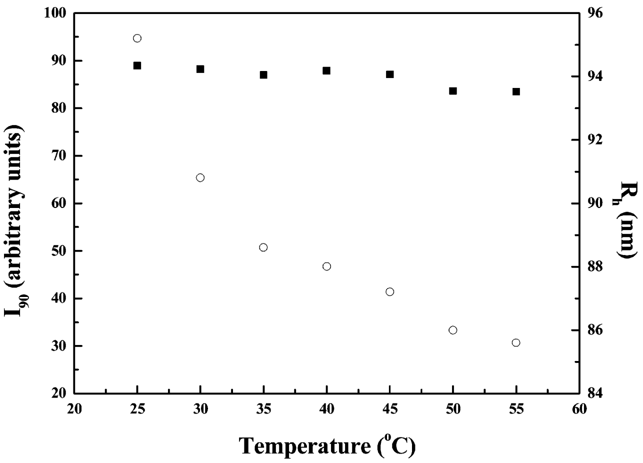

Figure 3. Temperature dependence of scattering intensity at 90° (■) and hydrodynamic radius (○) for NaBMA-5 micellar solution ($c_{pol} = 1.050 \times 10^{-4}$ g mL^{-1}) in water.

as a function of temperature for sample NaBMA-5 at a concentration of 5.2×10^{-4} g mL^{-1} are shown, depicts a representative example for spherical micelle behavior. In the temperature range studied light scattering intensity at 90° remains stable. This indicates that no change in the molecular weight (and aggregation number) of the micelles takes place. Additionally, polydispersity remains lower than 0.1 at all temperatures (not shown). This result should be expected due to the high hydrophobicity of the PB cores. On the other hand, the measured apparent hydrodynamic radius decreases as temperature increases. Presumably micellar size decreases due to a decrease in solvent quality with temperature. Breakage of the hydrogen bonds formed between water molecules and carboxyl groups of the corona may be the primary reason for the observed shrinkage. A change in the distribution of the counterions in the corona may also be operative, leading to different levels of charge within the corona, a situation that influences electrostatic interactions between chains. The data on the behavior of polyelectrolyte chains at different temperatures are limited (in order to have a more clear explanation on the observed behavior) presumably due to the complexity of polyelectrolyte systems in pure water. Further studies on this subject will be useful and are under way in our laboratory. The shrinkage amounts to more than 10% of the original size of the micelle at 25 °C. The effect is also seen in the other samples forming spherical micelles and does not seem to depend on copolymer concentration. A decrease in size of the low R_h population in the case of sample NaBMA-9 solutions with increasing temperature is also evident. The size of the large R_h component changes little with temperature. This may indicate that the effect of temperature is minimal for the large aggregates or changes in size are more difficult to be detected in this case. It is worth noting that both the overall intensity and the intensity ratios of the two peaks also remain unchanged with temperature.

Influence of NaCl Concentration. Since the behavior of polyelectrolytes in aqueous solutions is highly dependent on the presence and the amount of low molecular weight salt, we investigated the micellar characteristics of the copolymers at varying NaCl concentrations. The results are summarized in Table 5 for samples NaBMA-6, -3, and -9. The sample NaBMA-5 was insoluble in aqueous solutions containing NaCl in the indicated concentrations although its composition is similar to those of NaBMA-6 and NaBMA-3. This indicates that not only the composition but also the absolute molecular weight of the insoluble block plays a role in the solubility characteristics of amphiphilic block copolymers with a polyelectrolyte water-soluble block. The solvent quality toward polyelectrolytes in aqueous solutions decreases as the salt concentration increases. In the NaBMA-5 case the corona blocks are not solvated enough to keep the long PB block in solution.

For the rest of the samples aggregation numbers increase as soon as NaCl is present in solution. However, N_w changes little in the salt concentration range between 0.1 and 1.0 M. The results are in agreement with previous observations in similar systems.[26] Samples NaBMA-6 and NaBMA-3 continue to form spherical micelles in the salt solutions (Table 5). Micellar polydispersity remains at the range observed in pure water. The case of sample NaBMA-9 deserves special attention. Analysis of the correlation functions obtained from aqueous solutions of NaBMA-9 containing NaCl shows the existence of only one species in solution. μ_2/Γ^2 values are in the range of 0.25 (compared to values around 0.4 in the case of aqueous solutions in the absence of salt). An average R_h value in between the previous determined R_h's for the two different species present in aqueous solutions is obtained. This R_h is much lower than that of the population with the larger size in pure water. Additionally, the ratio R_g/R_h is larger than 1 at all NaCl concentrations investigated. Obviously the addition of salt dramatically changes the type of aggregates formed by this sample in aqueous solutions. Judging from the R_g/R_h and the polydispersity values, the presence of cylindrical micelles in aqueous solutions of NaBMA-9 containing NaCl is probable.[10] Such a shape change may be due to the increased screening of charges along the poly(sodium methacrylate) chains in the micellar corona. In the presence of NaCl, electrostatic repulsions are decreased and poly(sodium methacrylate) chains are less extended. This allows for an increase in the aggregation number (and the micellar core radius), demanding an increase in the PB stretching in the core. PB chains cannot stretch indefinitely, and at some point the shape of the micelle will change from spherical to cylindrical in order to accommodate the changes in the conformation of the core and corona chains. These shape transitions have been observed in similar block polyelectrolyte systems and studied by transmission electron microscopy but at higher copolymer concentrations than those used in this study.[25] Additionally, one cannot exclude the possibility of a

Table 5. Light Scattering Results for NaBMA Micelles in Aqueous NaCl Solutions

	0.1 M NaCl			0.5 M NaCl			1.0 M NaCl		
sample	N_w	R_g (nm)	R_h (nm)	N_w	R_g (nm)	R_h (nm)	N_w	R_g (nm)	R_h (nm)
NaBMA-6	356		17.9	350		17.3	350		17.8
NaBMA-9	2064	$41._1$	34.4	3156	$43._4$	34.7	3040	$44._5$	33.4
NaBMA-3	1392	$45._8$	74.3	1430	$46._1$	74.8			

frozen nature of the NaBMAA micelles. In this case the structural properties of the aggregates obtained may depend on the preparation protocol.

Conclusions

Well-defined diblock copolymers, having polybutadiene and poly(sodium methacrylate) blocks, synthesized by anionic polymerization and postpolymerization reactions, were found to form micelles with PB cores and PNaMAA coronas in dilute aqueous solutions. The aggregation characteristics and structure of the micelles were found to depend on the molecular characteristics of the block copolymers. Samples having a more asymmetric composition (lower PB content) formed spherical micelles, although the length of the PNaMAA block was rather short. At higher PB content (more symmetric composition) large aggregates were formed, together with normal micelles, which can be described as cylindrical micelles or micellar clusters. Increasing solution temperature resulted in a decrease in micellar dimensions, probably due to worsening of the thermodynamic solvent quality toward the polyelectrolyte coronas. Addition of NaCl to the aqueous systems was found to increase the aggregation numbers and sizes of the micelles. In the case of a sample with the highest PB content, experimental evidence points to the formation of cylindrical aggregates. The observations described in the present study may provide a means of manipulating the aggregate structure in dilute solutions, by changing the molecular characteristics of the copolymers and the physicochemical parameters of the system, according to the desired properties.

Acknowledgment. Financial support from the Research Committee of the University of Athens (Special Account for Research) and the European Human Potential-Research and Training Network HPRN-CT-1999-00151 (POLYNANO) is gratefully acknowledged. Fruitful discussions with Prof. A. Eisenberg are also gratefully acknowledged.

References and Notes

(1) Tuzar, Z.; Kratochvil, P. *Surf. Colloid Sci.* **1993**, *15*, 1.
(2) Hamley, I. A. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1998.
(3) Webber, S. E., Munk, P., Tuzar, Z., Eds.; *Solvents and Self-Organization of Polymers*; NATO ASI Series Vol. E327; Kluwer Academic Publishers: Dordrecht, 1996.
(4) Moffitt, M.; Khougaz, K.; Eisenberg, A. *Acc. Chem. Res.* **1996**, *29*, 95.
(5) Bahadur, P.; Sastry, N. V.; Marti, S.; Riess, G. *Colloids Surf.* **1985**, *16*, 337.
(6) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3276.
(7) Forster, S.; Zisenis, M.; Wenz, E.; Antonietti, M. *J. Chem. Phys.* **1996**, *104*, 9956.
(8) Nakano, M.; Matsuoka, H.; Yamaoka, H.; Poppe, A.; Richter, D. *Macromolecules* **1999**, *32*, 697.
(9) Ding, J.; Liu, G.; Yang, M. *Polymer* **1997**, *38*, 5497.
(10) Antonietti, M.; Heinz, S.; Schmidt, M.; Rosenauer, C. *Macromolecules* **1994**, *27*, 3276.
(11) Zhou, Z.; Chu, B. *Macromolecules* **1988**, *21*, 2548.
(12) Schillen, K.; Brown, W.; Johnsen, R. M. *Macromolecules* **1994**, *27*, 4825.
(13) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 7378.
(14) Iatrou, H.; Willner, L.; Hadjichristidis, N.; Halperin, A.; Richter, D. *Macromolecules* **1996**, *29*, 581.
(15) (a) Tsitsilianis, C.; Papanagopoulos, D.; Lutz, P. *Polymer* **1995**, *36*, 3745. (b) Tsitsilianis, C.; Sfica, V. *Macromol. Rapid Commun.* **2001**, *22*, 647. (c) Voulgaris, D.; Tsitsilianis, C. *Macromol. Chem. Phys.* **2001**, *202*, 3284.
(16) Ramzi, A.; Prager, M.; Richter, D.; Efstratiadis, V.; Hadjichristidis, N.; Young, R. N.; Allgaier, J. B. *Macromolecules* **1997**, *30*, 7171.
(17) (a) Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. *Macromolecules* **2000**, *33*, 1741. (b) Pispas, S.; Poulos, Y.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 4177. (c) Sotiriou, K.; Nannou, A.; Velis, G.; Pispas, S. *Macromolecules* **2002**, *35*, 4106.
(18) Alexandridis, P., Lindman, B., Eds. *Amphiphilic Block Copolymers. Self-Assembly and Applications*; Elsevier: Amsterdam, 2000.
(19) Jonsson, B.; Lindman, B.; Holmberg, K.; Kronberg, B. *Surfactants and Polymers in Aqueous Solutions*; J. Wiley & Sons: Chichester, 1998.
(20) Selb, J.; Gallot, Y. In *Developments in Block Copolymers*; Goodman, I., Ed.; Elsevier Applied Science: London, 1985; Vol. 2, pp 27−96.
(21) Forster, S.; Hermsdorf, N.; Bottcher, C.; Lindner, P. *Macromolecules* **2002**, *35*, 4096.
(22) (a) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728. (b) Zhang, L.; Eisenberg, A. *J. Am. Chem. Soc.* **1996**, *118*, 3168.
(23) Yu, K.; Zhang, L.; Eisenberg, A. *Langmuir* **1996**, *12*, 5980.
(24) (a) Astafieva, I.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7339. (b) Astafieva, I.; Khougaz, K.; Eisenberg, A. *Macromolecules* **1995**, *28*, 7127.
(25) Zhang, L.; Eisenberg, A. *Macromolecules* **1996**, *29*, 8805.
(26) Khougaz, K.; Astafieva, I.; Eisenberg, A. *Macromolecules* **1995**, *28*, 7135.
(27) Zhang, L.; Barlow, R. J.; Eisenberg, A. *Macromolecules* **1995**, *28*, 6055.
(28) Yu, Y.; Zhang, L.; Eisenberg, A. *Macromolecules* **1997**, *13*, 2578.
(29) (a) Qin, A.; Tian, M.; Ramireddy, C.; Webber, S. E.; Munk, P. *Macromolecules* **1994**, *27*, 120. (b) Ramireddy, C.; Tuzar, Z.; Prochazka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992**, *25*, 2541.
(30) (a) Tsitsilianis, C.; Voulgaris, D.; Stepanek, M.; Podhajeoka, K.; Prochazka, K.; Tuzar, Z.; Brown, W. *Langmuir* **2000**, *16*, 6868. (b) Tsitsilianis, C.; Alexandridis, P.; Lindman, B. *Macromolecules* **2001**, *34*, 5979.
(31) Guenoun, P.; Davis, H. T.; Tirrell, M.; Mays, J. W. *Macromolecules* **1996**, *29*, 3965.
(32) Xu, R.; Winnik, M. A.; Hallett, F. R.; Riess, G.; Croucher, M. D. *Macromolecules* **1991**, *24*, 87.
(33) Mortensen, K.; Brown, W.; Almdal, K.; Alami, E.; Jada, A. *Langmuir* **1997**, *13*, 3635.
(34) Poppe, A.; Willner, L.; Allgaier, J.; Stellbrink, J.; Richter, D. *Macromolecules* **1997**, *30*, 7462.
(35) Burke, S. E.; Eisenberg, A. *Langmuir* **2001**, *17*, 8341.
(36) Hecht, E.; Mortensen, K.; Gradzielski, M.; Hoffmann, H. *J. Phys. Chem.* **1995**, *99*, 4866.
(37) Zheng, Y.; Davis, H. T. *Langmuir* **2000**, *16*, 6453.
(38) Egger, H.; Nordskog, A.; Lang, P.; Brandt, A. *Macromol. Sump.* **2000**, *162*, 291.
(39) Pispas, S.; Hadjichristidis, N. *Langmuir* **2003**, *19*, 48.
(40) Won, Y.-Y.; Davis, H. T.; Bates, F. S. *Science* **1999**, *283*, 960.
(41) Bronstein, L.; Kramer, E.; Berton, B.; Burger, C.; Forster, S.; Antonietti, M. *Chem. Mater.* **1999**, *11*, 1402.
(42) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.
(43) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull. (Berlin)* **1986**, *15*, 127.
(44) Hautekeer, J. P.; Varshney, S.; Fayt, R.; Jacobs, C.; Jerome, R.; Teyssie, P. *Macromolecules* **1990**, *23*, 3893.
(45) Pispas, S.; Siakali-Kioulafa, E.; Hadjichristidis, N.; Mavromoustakos, T. *Macromol. Chem. Phys.* **2002**, *203*, 1317.
(46) (a) Schmidt, M.; Nerger, D.; Buschard, W. *Polymer* **1979**, *20*, 582. (b) Antonietti, M.; Bremser, N.; Schmidt, M. *Macromolecules* **1990**, *23*, 3796.

MA034627O