Polyelectrolyte Behavior of Polystyrene-*block*-poly(methacrylic acid) Micelles in Aqueous Solutions at Low Ionic Strength

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ABSTRACT: The polyelectrolyte behavior of kinetically frozen multimolecular polystyrene-*block*-poly-(methacrylic acid), PS-PMA, micelles has been studied in detail by a combination of light scattering, fluorescence correlation spectroscopy, and atomic force microscopy and by conductometry in aqueous solutions at low ionic strength. Experimental studies reveal important intermicellar electrostatic interactions. The experimental data are interpreted with help of computer studies, which combine mechanistic lattice Monte Carlo simulations and indirect treatment of electrostatic forces. The shell is modeled as a brush of self-avoiding chains tethered to the micellar core. Electrostatic interactions are obtained by solving the Poisson-Boltzmann equation.

Introduction

Di- and triblock copolymers form multimolecular micelles when dissolved in selective solvents (solvent for one type of blocks and a nonsolvent for the other type of blocks). If the solvent used is a mild selective solvent, i.e., it is not too strong a precipitant for one of blocks, micellization proceeds spontaneously upon dissolution of the copolymer in the solvent and obeys the scheme of closed association.¹ The reversible micellization represents the most typical self-assembling behavior of nonpolar copolymers in dilute solutions in organic selective solvents.²

Block polyelectrolytes containing one long polyelectrolyte block, e.g., poly(methacrylic acid), PMA, and one long and strongly hydrophobic block, e.g., polystyrene, PS, are insoluble in aqueous media, but fairly monodisperse micelles may be prepared indirectly. Upon dissolution of the sample in a judiciously chosen solvent mixture, e.g., a 1,4-dioxane-rich mixture with water, which is a mild selective precipitant for PS, multimolecular micelles with swollen PS cores and PMA shells form spontaneously and coexist in equilibrium with a small fraction of nonmicellized chains (unimers). The PS-PMA micelles may be transferred in aqueous media by stepwise dialysis against solvents with increasing water content.^{3a} During dialysis, the association number increases up to ca. 50% of water content (depending on the lengths of blocks). This "critical mixture" is an extremely strong precipitant for PS, and the micellization equilibrium freezes due to the fact that the PS cores of micelles become very compact and the exchange of unimers between PS-PMA micelles stops.^{3b} Since the critical micelle concentration for high molar mass copolymers is very low (it is not measurable by SLS and other common polymer techniques) and decreases with solvent selectivity,^{1,2} we assume that the unimer concentration for di- and triblocks is virtually zero. The association number of frozen micelles does not change with a further increase in water content and only the cores slightly shrink.^{3c} Some authors reported changes in the distribution of sizes of micelles kept in mixed solvents (namely micelles based on a polystyrene-poly-(2-vinylpyridine), PS-PVP, copolymer) with time.⁴ We have been using the stepwise dialysis fairly successfully for reproducible preparation of PS-PMA and PS-PVP micelles from dioxane-water and dioxane-methanolwater mixtures and we did not observe any changes of micelles formed by "well-behaving", i.e., for impurityfree and low-polydispersity samples in mixed solvent over a period of several weeks.⁵ Nevertheless, it is fair to say that some copolymers synthesized at the University of Texas in 1991–1992 did show changes with time, mainly in mixed solvents close to the "critical solvent composition". However these samples were not used in our studies.^{3,5a-c}

Since the glass transition temperature $T_{\rm g}$ for PS is ca. 100 °C, the nonswollen PS cores in water are essentially glassy at ambient temperatures. It is important to realize that the association number of kinetically frozen block polyelectrolyte micelles in aqueous media is not controlled by interactions with water molecules, but is a result of thermodynamic conditions that exist in the "critical solvent" in which the micellization process freezes. The kinetically frozen micelle in water may be regarded as an inert PS core decorated with a PMA brush. The stability and properties of aqueous solutions of PS-PMA micelles are controlled by the polyelectrolyte behavior of the PMA shell.

Thanks to promising potential applications of polymeric micelles in aqueous media, such as targeted drug delivery, removal of pollutants from water, etc., the behavior of water-soluble micelles has been the subject of numerous studies of many research groups. We have systematically studied the micellization of PS-PMA and PS-PVP copolymers and the structure and properties

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of their shells for more than 10 years.⁵ Other research groups have studied micelles with polyacrylic and polymethacrylic shells,⁶ polycationic shells based on aliphatic tertiary amines,⁷ micelles with neutral poly-(ethylene oxide) shells, such as polystyrene *block*-poly-(ethylene oxide)^{8a,b} or poly(propylene oxide)-*block*-poly-(ethylene oxide)^{8c-j} or poly(butylene oxide)-*block*-poly-(ethylene oxide),^{8a,g} modified micelles with cross-linked cores or shells,⁹ etc.¹⁰ Recently, some groups studied also the reversible (i.e., not kinetically frozen) polyelectrolyte micelles with cores formed by relatively short hydrophobic blocks above $T_{\rm g}$.¹¹

Despite numerous papers published on this subject in the past decade, studies of the polyelectrolyte behavior of micelles at low ionic strength are few. Some experimental observations have been mentioned as a topic of secondary interest in papers aimed at different aspects of the micellization behavior^{5d} and several theoretical papers have been devoted to this subject¹² although the kinetically frozen high molar mass polyelectrolyte micelles with shells formed by polyacids or polybases are suitable objects for studying polyelectrolyte behavior. Both the coarse-grain properties controlled by the long-range interparticle interactions and the fine-grain features due to the polyelectrolyte brushlike properties of shells contribute to rich and complex behavior of PS-PMA micelles at low ionic strength. Hence the polyelectrolyte behavior represents a challenging topic for a combined theoretical and experimental study.

Experimental Section

Materials. Copolymer. The polystyrene-*block*-poly(methacrylic acid) diblock copolymer was synthesized by Dr. C. Ramireddy at the University of Texas at Austin. First, a nonpolar polystyrene-*block*-poly(*tert*-butyl methacrylate) was prepared by an anionic polymerization in tetrahydrofuran at -78°C using cumylpotassium as initiator. The sample was hydrolyzed in 6 N HCl, purified, freeze-dried, and characterized by static light scattering, size exclusion chromatography, and NMR. All steps were described in detail in our earlier papers.^{5b} The weight-average molar mass was measured by SLS, $M_w =$ 39 600 g/mol, the polydispersity was measured by SEC, $M_w/M_n = 1.12$, and the mass ratio of PS was estimated by ¹H NMR, $w_{\rm PS} = 0.52$.

Fluorophore. Octadecylrhodamin B (ORB) was purchased from Molecular Probes, Ltd., Eugene, Oregon and used as obtained.

Solvents and Chemicals. 1,4-Dioxane, analytical grade, from Fluka Int. was used as obtained.

Carefully deionized water was used in the study. Its quality was controlled by conductometric measurements. The stock water and all aqueous solutions were stored in PET bottles to prevent the contamination with alkaline ions. The content of $\rm CO_2$ was minimized by bubbling the aqueous solutions with Ar. All dialyses were performed under N_2 atmosphere.

NaOH and NaCl, analytical grade, from Fluka Int. were used for preparation of aqueous solutions.

Preparation of Micellar Solutions. The solutions of micelles were prepared in a 1,4-dioxane-rich mixture with water and transferred by stepwise dialysis in solutions with increasing content of water and finally in pure water. In the last stage, 10 mL of each micellar solution was carefully dialyzed five times against 1000 mL of deionized water in PET bottles to remove all traces of small (mostly alkaline) ions. The final solutions of micelles were kept in PET bottles enclosed in the glass containers to prevent the contamination with alkaline ions and to minimize the diffusion of gases from outside.

Solutions containing different concentrations of either NaCl or NaOH, i.e., micelles with partially neutralized shells by NaOH were prepared by dialyzing micellar solutions against an excess of solutions with known concentrations of NaCl or NaOH in N_2 atmosphere. To study the behavior of weak acids, it is essential to prevent the contamination with CO₂, which results in formation of carbonates. Concentration changes during dialysis were determined by conductometry. They allow for determining the degree of ionization of PMA shells as a function of the bulk pH.

Techniques. Quasielastic Light Scattering (QELS). An ALV 5000 multibit, multiau autocorrelator (ALV, Langen, Germany) and an He–Ne laser ($l\lambda = 633$ nm) were employed. The solutions for measurements were filtered through 0.22 μ m Acrodisc filters. Measurements were performed with solutions of different concentration (0.001–7.0 mg/mL) at different angles and temperature 20 °C. Analysis of the data is based on the electrical field correlation function, $g_1(t)$, which can be written as an inverse Laplace transform (ILT) of the relaxation time distribution, $\tau A(\tau)^{13}$

$$g_1(t) = \int \tau A(\tau) \exp(-t/\tau) \,\mathrm{d}(\ln \tau) \tag{1}$$

where t is the lag-time. The relaxation time distribution, $\tau A(\tau)$, is obtained with the aid of a constrained regularization algorithm (REPES),¹⁴ which minimizes the sum of the squared differences between the experimental and calculated $g_2(t)$. The individual mean diffusion coefficients, D, are calculated from the second moments of the peaks as $D = \Gamma/q^2$ where $q = (4\pi n_0/\lambda) \sin(\theta/2)$ is the magnitude of the scattering vector and $\Gamma = 1/\tau$ is the relaxation rate. Here θ is the scattering angle, n_0 the refractive index of pure solvent, and λ the wavelength of the incident light. If needed, the average diffusion coefficient and polydispersity were evaluated using the cumulants method. The hydrodynamic radius $R_{\rm H}$ was evaluated from the diffusion coefficient using the Stokes–Einstein formula. The viscosities and refractive indices of 1,4-dioxane–water mixtures (for the evaluation of $R_{\rm H}$ values) were determined in previous studies.⁵

Static Light Scattering (SLS). The measurements were performed on an ALV 5000 instrument equipped with a He–Ne laser at 20 °C. Data were treated by the standard Zimm method.¹⁵ The refractive index increments, dn/dc, were measured on a Brice-Phoenix differential refractometer in our earlier studies. In the case of solutions containing NaCl or NaOH (i.e., for the partially neutralized micelles), the refractive index increments, $(dn/dc)_{\mu}$ were estimated at the osmotic equilibrium of low-molar-mass components.¹⁶

In the Zimm approach, the static light scatterings are treated by the equation

$$\frac{Kc}{R^{\rm cor}(q,c)} = \frac{1}{p(q,c)} \left(\frac{1}{M_{\rm w}} + 2A_2c + \dots \right)$$
(2)

where $K = 4\pi^2 n^2 (dn/dc)^2 \lambda^4 N_A$ is a constant containing the refractive index n of the solvent, the refractive index increment of the polymer with respect to the solvent, (dn/dc), wavelength of the light, λ , and the Avogadro constant $N_{\rm A}$. Further definitions are as follows: $R^{cor}(q,c)$ is the corrected Rayleigh ratio which depends on the polymer concentration and on the scattering vector \boldsymbol{q} with the absolute value $q = (4\pi/\lambda) \sin(\theta/\lambda)$ 2), where θ is the scattering angle, $M_{\rm w}$ is the weight-average molar mass of scattering polymeric particles, A_2 is the second virial coefficient of the concentration expansion, and p(q,c) is the scattering function which takes into account the interference effects. In practice, intensity I^{cor} of the scattered light is measured relative to a standard (usually toluene) and plotted instead of the Rayleigh ratio. In such a case, K reflects also the recalculation factors, apparatus constants and correction terms. In our earlier studies, we measured (dn/dc) for PS-PMA micelles in water and increments at osmotic equilibrium of the low molar mass components, $(dn/dc)_u$ in NaCl solutions and in aqueous buffers for micelles differing in PS/PMA composition. We have found a linear dependence of (dn/dc) on the copolymer composition and confirmed that the increment may be calculated as a weighted average of contributions from individual blocks.5p-r All light scattering measurements were performed in quartz cuvettes. Solvent from the dialysis bath was used for diluting the solutions for light scattering measurements, which is needed to maintain Donnan equilibria and optical conditions undisturbed.⁵⁰

Fluorescence Correlation Spectroscopy. All measurements were performed with a binocular microscope ConfoCor I, Carl Zeiss, Jena, Germany, equipped with a 514 nm argon laser, an adjustable pinhole together with a special fluorescence optics, SPCM-200PQ detection diode and an ALV-5000 correlator (ALV, Langen, Germany). FCS is a technique in which temporal fluctuations in the fluorescence intensity measured from a sample of fluorescent molecules are analyzed to obtain information about processes that give rise to fluorescence fluctuations.¹⁷ In this work we are interested only in the translational diffusion and photobleaching (due to the intersystem crossing) as a complicating process. If a roughly cylindrical volume of the radius w_1 and height $2w_2$, which contains two types of fluorescent particles with quantum yields and absorptivities q_1, q_2 and A_1, A_2 , respectively, and the same probabilities of the intersystem crossing (typically, a system containing a mixture of bound and dispersed fluorophores), is irradiated by a focused laser beam with Gaussian intensity profile, the normalized autocorrelation function of fluorescence fluctuations, G(t), assumes the following form^{17d}

$$G(\tau) = 1 + \frac{1}{N(1-Y)} \{1 - T(1 - e^{-\tau/\tau_0})\} \times \left\{ \frac{1-Y}{1+(\tau/\tau_1)} \frac{(A_1q_1)^2}{[1 + S^{-2}(\tau/\tau_1)]^{1/2}} \frac{Y}{1+(\tau/\tau_2)} \frac{(A_2q_2)^2}{[1 + S^{-2}(\tau/\tau_2)]^{1/2}} \right\} (3)$$

where N is the particle number (i.e., total number of fluorescent particles in this volume), Y and (1 - Y) are molar fractions of both species, T is the fraction of molecules converted to the triplet state, τ_0 is the characteristic time for the transition (τ_0^{-1}) is the transition rate), S is the ratio of half-axes, $S = w_2/w_1$, and the irradiated volume is $V = 2pw_1^2w_2$. Diffusion coefficient of the *i*th component, D_i , may be calculated as $D_i = w_1^2/4t_1$, and the hydrodynamic radius can be recalculated using the Stokes–Einstein formula, $R_{\rm H} = kT/(6pDh)$, where k is the Boltzmann constant, T is the temperature, and h is the viscosity of the solvent.

Atomic Force Microscopy. All measurements were performed in the tapping mode under ambient conditions using a commercial scanning probe microscope, Digital Instruments NanoScope dimensions 3, equipped with a Nanosensors silicon cantilever, typical spring constant 40 N m⁻¹. Polymeric micelles were deposited on a fresh (i.e., freshly peeled out) mica surface (flogopite, theoretical formula KMg₃AlSi₃O₁₀(OH)₂, Geological Collection of Charles University in Prague, Czech Republic) by a fast dip coating in a dilute micelle solution in dilute alkaline buffer ($c_{\rm P}$ ca. 10⁻² g L⁻¹). After the evaporation of water, the samples for AFM were dried in a vacuum oven at ambient temperature for ca. 5 h.

Conductometry. Conductivity of NaOH solutions before and after dialysis (for determination of the degree of neutralization of PMA shell in Donnan equilibrium) were measured with precision conductivity equipment consisting of a Radiometer CDM2 apparatus and a conductivity cell with cell constant 1.53 cm⁻¹. The water used for the study had a conductivity approximately $1.0 \times 10^{-6} \Omega^{1-} \text{cm}^{-1}$.

Theoretical Part

Model. In our recent papers, we studied the behavior of shells of kinetically frozen micelles in aqueous and polar media by SCF calculations and by MC simulations.¹⁸ We developed a suitable model of the polyelectrolyte shell formed by a weak polyelectrolyte,^{18c} which we use for the analysis and interpretation of the experimentally observed behavior.

(1) We use a Monte Carlo simulation¹⁹⁻²¹ on a simple cubic lattice and model very dilute solution of kinetically frozen micelles, i.e., we study the shell behavior of a single micelle only. The association number is taken

from the experiment. The size of the core, lattice constant (i.e., the size of the "lattice Kuhn segment") and the effective number of lattice segments is recalculated from pertinent experimental values on the basis of the coarse graining parametrization described in detail in our earlier papers.¹⁸

(2) The segment-segment and segment-solvent interactions are described by contact interactions between nearest beads (or free lattice sites-in the case of the solvent). In this study, we have slightly changed the parameters describing the interactions of PMA beads with beads representing either the aqueous solvent or other components in order to reflect the well-known behavior of linear PMA in water.²² We use the most common matrix of interaction parameters in which the "reference interactions", i.e., those where solvent is involved, are set to zero. The following parameters were used: $\epsilon_{S-S} = 0$, $\epsilon_{PMA-S} = 0$, $\epsilon_{C-S} = 0$, $\epsilon_{PMA-PMA} = -0.27$, and $\epsilon_{\text{PMA-C}} = 0.8$ ($\epsilon_{\text{C-C}} = 0.8$), where S, C, and PMA stand for solvent (i.e., an empty lattice site, occupied implicitly by solvent), C core (lattice point at the surface of the core), and the PMA bead (i.e., the Kuhn lattice segment, irrespectively of the ionization).

(3) The electrostatic interactions are treated indirectly by solving the spherically symmetrical Poisson–Boltzmann equation (PBE) for the electrostatic potential $\phi(r)$ as a function of the distance from the center of the micelle²³

$$\frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(r^2 \frac{\mathrm{d}\phi}{\mathrm{d}r} \right) = \frac{\rho}{\epsilon_0 \epsilon_\mathrm{r}} \tag{4}$$

where ϵ_0 and ϵ_r are the dielectric vacuum permittivity and the relative (position dependent) permittivity of the dielectric medium. The charge density $\rho(r)$ includes both the charge of the macroion (micelle) and of all small ions

$$\rho = \sum_{i} q_{e} z_{i} [x_{i}] c_{0} N_{A}$$
(5)

where q_e is the elementary charge, z_i is the charge number, $[x_i]$ are the relative concentrations of individual charged species, $c_0 = 1$ mol/L is the standard concentration, and N_A is the Avogadro constant.

Details of the Solution. For solving the PBE, we consider the following components of the system: -COOH, $-COO^-$, H_3O^+ , OH^- , Na^+ , and Cl^- . Not all of these are independent since

$$K_{\rm w} = a_{\rm H_3O^+} a_{\rm OH^-}$$
 and $K_{\rm A} = \frac{a_{\rm H_3O^+} a_{-\rm COO^-}}{a_{-\rm COOH}}$ (6)

where $K_{\rm w}$ and $K_{\rm A}$ are the ionization product of water and the effective dissociation constant describing the dissociation of carboxylic groups in PMA, respectively. The latter parameter is actually not constant because the abbility of carboxylic groups bound to a polyelectrolyte chain to dissociate depends on the actual degree of dissociation in their vicinity, and $K_{\rm A}$ generally decreases with an increasing charge on the macroion. The effective dissociation constant for poly(methacrylic acid) in solutions with changing ionic strength and degree of ionization was measured by Morcellet et al.^{24a} and by Porasso et al.^{24b} Nevertheless, we use the constant value $pK_{\rm A} = 4.69$ for the monomeric methacrylic acid as a rough, although reasonable first approximation.²⁵ We are aware that a fairly high constant $K_{\rm A}$ used in simulations overestimates the dissociation. However, most simulations and theoretical calculations for polyelectrolytes use $pK_{\rm A}$ for the monomeric unit, and they give reasonable results at the semiquantitative level.

The activities of components a_i are calculated using the Debye–Huckel limiting law.²³

The only independent parameters used in our simulations are: pH and ionic strength $I = \sum^{1/2} [x_i] z_i^2$, which control the concentration of small ions in the bulk (for $r \rightarrow \infty$) and may be adjusted by the addition of HCl and NaOH, only. The electrostatic potential is zero at infinity (i.e., at a sufficient distance from the micelle) and hence the position-dependent concentrations of small ions may be expressed according to the Boltzmann theorem as follows

$$[x_i(r)] = [x_i]_{\infty} \exp\left[\frac{-q_e z_i \phi(r)}{kT}\right]$$
(7)

When the position-dependent concentration of H_3O^+ is substituted in the definition of the dissociation constant K_A (eq 6), using $[-COO^-] = \eta - [-COOH]$, where η is the position-dependent concentration of PMA segments, which we obtain by Monte Carlo simulation, we get

$$[-\text{COO}^{-}(r)] = \frac{\eta}{1 + [\text{H}_{3}\text{O}^{+}(r)]_{\infty} \exp[-q_{e}\phi(r)/kT]\gamma_{+}\gamma_{-}/K_{\text{A}}}$$
(8)

where γ_+ and γ_- are the Debye–Huckel activity coefficients of H₃O⁺ and –COO⁻, respectively. This formula together with the Metropolis criterion (in which both the short-range and long-range electrostatic interactions are combined) actually bridges the indirect treatment of electrostatic forces with the mechanistic Monte Carlo simulation. In the end, we may write the following expression for the position dependent charge density

$$\rho(r)/q_{e}c_{0}N_{A} = I_{\infty}(-e^{q_{e}\phi/kT} - e^{q_{e}\phi/kT}) - \frac{\eta}{1 + [H_{3}O^{+}(r)]_{\infty} \exp[-q_{e}\phi(r)/kT]\gamma_{+}\gamma_{-}/K_{A}}$$
(9)

which can be inserted in the rhs of eq 4. Then the differential equation 4 is solved numerically (for details see ref 18), and the electrostatic potential $\phi(r)$ is used for the calculation of the contribution of electrostatic potential energy in the Metropolis acceptance criterion.

Results and Discussion

Fluorescence Correlation Spectroscopy Study. Several samples of kinetically frozen PS-PMA micelles differing in molar mass and size were prepared and their solution behavior was studied in pure water and in solutions containing increasing concentrations of NaCl and NaOH. Two samples: small micelles M1 and large micelles M2 were used for the detailed study of the solution behavior and therefore were carefully characterized by a combination of several experimental techniques. Fluorescence correlation spectroscopy was used for the measurement of number-average molar masses of micelles, M_n . This measurement is very straightforward, accurate, and reliable, because it does not require fitting the autocorrelation function of fluctuations to a theoretical expression. The principle of M_n



Figure 1. Titration curve of M1 micelles by octadecylrhodamine B for determining the number-average molar mass, $M_{\rm n}$, by fluorescence correlation spectroscopy. Symbol N stands for the "particle number", i.e., the average number of labeled micelles in the active irradiated volume, and $c_{\rm ORB}$ is the concentration of octadecylrhodamine B in the solution. Concentration of the copolymer: $c_{\rm p} = 6.5 \times 10^{-3}$ mg/mL.

evaluation is based on monitoring the average frequency of fluctuations, which are caused by the diffusion of particles in and out of the irradiated volume. Hence the average frequency of fluctuations is proportional to the number of fluorescent particles *N* in the active volume. The measurement, which is so far only little used in polymer chemistry, may be briefly outlined as follows. The micellar solution is slowly titrated with the solution containing a fluorescent probe that binds strongly to micelles and the average frequency of fluctuations is measured as a function of the probe concentration, $c_{\rm F}$ (after the equilibration, which may take a fairly long time and the necessary time must be estimated before the measurement). At $c_{\rm F}$ lower than the concentration of micelles, $c_{\rm mic}$, individual probes bind to different micelles and the number of fluorescent species in the active volume (i.e., in the irradiated volume corrected by spatially changing intensity of the laser beam) increases and hence the frequency of fluctuations also increases. When all micelles are labeled on average by one probe, more probes start to bind to some micelles. The fluctuations become larger, but their frequency remains constant because the number of fluorescent species does not change any more. The aforementioned simplified description leads to an idealized experimental curve consisting of two straight lines: (i) a linearly rising first part for low $c_{\rm F}$ and (ii) a constant part for high $c_{\rm F}$. The leveling-off part of the curve yields the number of fluorescent species, i.e., the number of micelles in the active volume. From the number of labeled micelles, volume and polymer concentration, the numberaverage molar mass of micelles may be calulated. The experimentally measured curves are smooth and their shape is sometimes quite complex due to the Poisson distribution of probes among micelles and other effects. We have shown in our recent papers, that the limiting part of the curve for high $c_{\rm F}$ provides correct values of $M_{\rm n}$, even if various complicating effects, such as impurity quenching, cannot be neglected.^{5m} The titration curve for small micelles, M1, is shown in Figure 1.

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Nevertheless, this study revealed a significant limitation of this technique for large nanoparticles. Large micelles may be labeled by several fluorophores at different and quite distant places. When the micelle moves out or into the irradiated volume, several smaller fluctuations may be registered instead of a large one and the calculated molar mass may thus differ considerably from the true value. We believe that this effect is responsible for an unrealistically large difference between M_w and M_n for large micelles, M2, which was not confirmed by AFM.

The Characterization of Micelles by AFM. To obtain detailed information on the distribution of micellar sizes, we performed atomic force microscopy study (tapping mode, TM AFM) for both types of micelles deposited on a mica surface. In our earlier papers, we have shown that PS-PMA micelles can be deposited on the freshly prepared (i.e., pealed off) mica surface by dip coating in micellar solutions of suitable concentration without significant aggregation of micelles at the surface.⁵⁽¹⁾ Micelles are deformed after the deposition (pancake-formed), but both the radius, R, and the height, z, of the micelles are proportional to the size of the micelles in the solution. The height is actually proportional to the size of the core. A histogram based on the section analysis for several hundreds of micelles provides a reasonable estimate of the distribution function of micellar sizes and molar masses. Figure 2a shows a large 4 μ m \times 4 μ m scan (the top view) for surface deposited M1 micelles. Figure 2b shows the distribution of the radii (the left part) and the heights (the right part) of deposited M1 and M2 micelles, respectively. If we assume that the molar masses of micelles are proportional to the product R^2z , we may reconstruct the weight and number distributions of molar masses (using the mass average molar masses, $M_{\rm w}$, measured by SLS). The number distributions $f_n(M)$ for M1 and M2 micelles based on several hundreds of micelles are shown in Figure 2c. The polydispersity index $M_w/M_n = 1.15$ for small micelles M1 compares fairly well with that based on values obtained from a combination of SLS and FCS.

Study of the Polyelectrolyte Behavior by SLS and QELS. Light scattering was used for the characterization of micelles under reference conditions (pH 9.2, I = 0.15) and for the systematic study of the solution behavior of micelles. The characteristics of small micelles M1 and large micelles M2 obtained by FCS, AFM, SLS, and QELS under reference conditions are summarized in Table 1. Experimental data on the solution behavior for two selected systems (small, M1, and large micelles, M2) are presented. The first data series presents SLS results for large M2 micelles in solutions containing NaCl. The studied solutions contained 0.0, 1.0×10^{-5} , 1.0×10^{-4} , 1.0×10^{-3} , 1.0×10^{-2} , and 1.0^{-2} imes 10⁻¹ mol/L of NaCl. Parts a–c of Figure 3 show Zimm plots for solutions with $c_{\text{NaCl}} = 0.0, 1.0 \times 10^{-4}$, and 1.0 \times 10⁻² mol/L, respectively.

The analysis of the data is based on the scattering function $p(q,c) = I^{\text{cor}}(q)/I^{\text{cor}}(q=0)$ in eq 2, which takes into account interference effects, due to the intraparticle and interparticle correlations. The studied micelles are spherical and we assume that the scattering function p(q,c) can be expressed as the product of the single particle form factor P(q), reflecting the interference of light rays scattered at different parts of the same particle and the solution structure factor S(q,c) reflect-



Figure 2. (a) Atomic force microscopy micrograph of M1 micelles deposited on mica surface (top view of a large 4 μ m × 4 μ m scan). (b) Histograms of radii, *R* (the left part), and heights, *z* (the right part), of the surface-deposited micelles M1 and M2, based on the section analysis of 300 micelles. (c) Number distributions, $f_n(M)$, of micellar molar masses of M1 and W2 micelles, respectively, calculated from the horizontal and vertical dimensions measured by AFM.

ing the interference of rays scattered from segments of different particles in the solution, i.e., p(q,c) = P(q)S(q,c). This relation is strictly valid only in a system of

Table 1. Characterization of Micelles Determined by QELS, SLS, FCS, and AFM (in 0.05 M Borax Solution)

samnle	$M_{ m w}/ m kg$	$M_{ m n}/ m kg$	R_{11}/nm^a	R / nm^b	M /M d	M /M b,
Sample	mor	mor	ItH/IIII	nginn	M W/M n	M W/M n
M1	$3.0 imes10^3$	$2.3 imes 10^3$	30.0		1.15	1.30
M2	$31.0 imes 10^3$		64.5	58.5	1.24	
^a QELS. ^b SLS. ^c FCS. ^d AFM.						

homogeneous monodisperse spheres, but it has been used in the overwhelming majority of studies of similar systems.²⁷

The Zimm plots in Figure 3, parts a and b, show strongly curved $Kc/I^{cor}(q,c)$ vs q dependences for micellar concentrations higher than 0.1 mg/mL. They decrease with increasing q and pass through a minimum. This shape indicates strong electrostatic interactions between micelles. For solutions of low ionic strength, i.e., for c_{NaCl} = 0.0 and 1.0 \times 10⁻⁵ mol/L, we evaluate the solution structure factors S(q,c) as functions of q. For the accurate evaluation of the structure factor, the form factor P(q) should be known.²⁷ In our case, the formula for homogeneous spheres cannot be used since micelles are not homogeneous spheres.^{5d-g} To avoid complications, we used a simple, but generally recognized approach which consists of the normalization of $I^{cor}(q,c)/c$ values by $(I^{cor}(q,c)/c)_0$ for low c. This approach assumes that $S(q,c) \approx 1$ for low c and any q, and it usually gives better results than the approach based on the use of the limiting formula $P(q)^{-1} = 1 + (1/3)\langle R_g^2 \rangle_z q^2$. The values of the *z*-average radius of gyration, $\langle R_g^2 \rangle_z$ were obtained from measurements at the three lowest micellar concentrations which obey a linear relationship between $Kc/I^{cor}(q,c)$ and q and yield reasonable $\langle R_g^2 \rangle_z$ values. The pertinent values are very close to the value measured under reference conditions, i.e., for pH 9.2 and I = 0.15, the following values were obtained: $\langle R_g^2 \rangle_z = 56.8$ nm for $c_{\text{NaCl}} = 0.0$, $\langle R_g^2 \rangle_z = 56.6$ nm for 10^{-4} , and $\langle R_g^2 \rangle_z = 58.6$ nm for 1.0×10^{-2} mol/L. There is still a problem regarding the size of micelles and the reference system for the evaluation of structural factor, S(q,c). The expansion of charged shells depends on electrostatic interactions. Both the intraand intermicellar interactions affect the state of the shell. Hence the true geometrical size of micelles may change slightly with intermicellar distances, i.e., with dilution.

The structure factors S(q,c) for several micellar concentrations of salt-free M2 solutions are shown in Figure 4a. The well-pronounced maxima, which shift to higher q with increasing micellar concentration, indicate considerable interparticle interactions. Unfortunately the restricted range of q values, which is accessible in light scattering experiments, does not yield the required part of the S(q,c) vs q curve and does not allow calculation of the radial distribution function g(c,r) for the micelles. Nevertheless the measurement allows an estimate of the average distances of nearest neighbors, $\langle r \rangle_{\rm exp}$, since $\langle r \rangle_{\rm exp} = 2\pi/S^{\rm max}(q,c).^{27}$ For the salt-free solution with polymer concentration $c_{\rm P} = 1.04$ mg/mL, the evaluation yields a reasonable average distance $\langle r \rangle_{exp}$ ca. 350 nm, which compares well with the distance for the same concentration of micelles arranged in a simple cubic lattice. A regular cubic arrangement was assumed for simple comparison.

Average distances between the closest neighbors, $\langle r \rangle_{exp}$ in both systems are plotted in Figure 4b as a function of polymer concentration (log-log plot). The dotted



Figure 3. Zimm plots Kc/R vs $(q^2 + kc)$ for large M2 micelles in aqueous solutions differing in NaCl concentration $(k = -2 \times 10^3)$: (a) $c_{\rm NaCl} = 0.0$; (b) $c_{\rm NaCl} = 1.0 \times 10^{-4}$ mol/L; (c) $c_{\rm NaCl} = 1.0 \times 10^{-2}$ mol/L. The measurements were performed for scattering angles from 30 to 150° for micellar solutions in the concentration range 2.5 $\times 10^{-3}$ to 2.0 mg/mL. *K* is the apparatus constant which includes also the square of the refractive index increment, $(dn/dc)^2$, *c* is the polymer concentration, *R* is the corrected Rayleigh ratio, *q* is the scattering vector of the length, $q = (4\pi/\lambda) \sin(\theta/2)$, and *k* is an appropriate constant.

curve shows theoretical distances for a simple cubic arrangement. The correlation is persuasive in both systems. The curves do not overlap, but they are close and fairly similar to each other. The comparison of results for M1 and M2 micelles suggests a sort of universal solution behavior of strongly interacting micelles, which depends (for comparably charged micelles)



Figure 4. (a) Structure factors, S(q,c), for salt-free solutions of polyelectrolyte micelles M2 for polymer concentrations: c = 2.08 mg/mL (curve 1), c = 1.04 mg/mL (curve 2), c = 0.52 mg/mL (curve 3), and c = 0.26 mg/mL (curve 4). (b) The average distances of the nearest pairs of micelles M1 (curve 2, \bullet) and M2 (curve 1, \blacksquare) obtained from the first maximum of the structure factor, S(q,c), as functions of the micellar molar concentration c_{mic} . The dashed curve shows theoretical distances of micelles arranged hypothetically in the simple cubic lattice.

mainly on intermicellar distances and only little on micellar sizes.

Recent measurements with highly charged spherical microgels indicate that highly structured solutions may undergo phase transitions depending on concentration.²⁸ At low concentrations, fairly concentrated regions coexist in equilibrium with dilute regions, while at higher concentrations only one highly ordered phase is stable. Our data do not indicate phase separation at low concentrations. This is understandable since electrostatic interactions, although important in our system, are much weaker then those in systems of microgels containing strong acid $-SO_3^-$ groups and the solubility of PS-PMA micelles is primarily determined by the solubility of the flexible shell-forming PMA chains in aqueous media. Hence the electrostatic stabilization of dissolved micelles plays only a secondary role.

QELS measurements show strong polyelectrolyte effects in salt-free solutions. In all cases, a single relaxation mode, which depends on concentration, is observed. Angular measurements show strong deviations from the diffusion-controlled behavior; i.e., the experimental relaxation time does not depend linearly on $\sin^2(\theta/2)$ (see Figure 5) and the shapes of curves τq^2 vs q follow the structure factor obtained by SLS.

Dependences of Micellar Characteristics on the Degree of Ionization. We have earlier shown that the



Figure 5. Correlation time τ measured by QELS multiplied q^2 , i.e., the product τq^2 as a function of the scattering vector q for the salt-free solutions of M2 micelles for concentrations of the polymer c = 2.08 mg/mL (curve 1), c = 1.04 mg/mL (curve 2), c = 0.52 mg/mL (curve 3), and c = 0.26 mg/mL (curve 4).

determination of the degree of neutralization of carboxylic groups in PMA shells is a complex, difficult, and time-consuming task.^{5g} Computer studies and numerous indirect results of our experimental studies indicate that the local (equilibrium) dissociation of PMA does not correspond to the bulk pH and changes with the position in the shell due to Donnan equilibria and that the equilibration is very slow.

In this study, we determined the degree of neutralization of -COOH groups as a function of the bulk pH by dialysis against NaOH solutions. We dialyzed a small volume of the solution of PS-PMA micelles against an excess of fairly dilute NaOH solution (at the precisely known concentration in the region 1.0 imes 10⁻⁵ to 1.0 imes 10^{-3} mol/L) under a N₂ atmosphere. From the concentration decrease of the base in the dialyzation bath (i.e., from NaOH consumption for the actual neutralization) and the volume changes during dialysis, we evaluated the overall degree of neutralization of PMA (which corresponds to the dissociation of -COOH groups) at Donnan equilibrium as a function of bulk pH. The concentration changes in the dialyzation bath were determined by conductometric measurements. The degree of -COOH neutralization, ξ_n is plotted in Figure 6 as a function of the bulk pH. It is evident that in neutral and slightly basic solutions, i.e., in the pH range between 9 and 10, the degree of neutralization is still quite low and it rises steeply at pH higher than 10. The dashed curves (2) and (3) show the theoretical behavior for $pK_A = 6.3$ and $pK_A = 4.69$, respectively.^{24,25} It is evident that the simulated dissociation is strongly overestimated in both cases, which is understandable because we use a relatively large value of the effective dissociation constant. As explained in the Theoretical section, we use a constant pK_A for the monomeric methacrylic acid on purpose since an effective (i.e., dissociation-dependent) dissociation constant may obscure basic trends and important features of the studied system. Despite the fact that the individual curves are displaced on the pH scale, all basic trends compare well. The inset shows the experimental degree of neutralization as the function of the base concentration in bulk solvent.

The polyelectrolyte behavior of partially neutralized PS-PMA micelles is worth mentioning. At first, the neutralization of a low fraction of carboxylic groups (ca.



Figure 6. Degree of neutralization of M1 micelles ξ_n , evaluated by conductometry after dialysis as a function of pH of the dialyzation bath (i.e., the bulk pH). Experimental data: solid curve (1). Simulation data: $pK_A = 6.3$, dashed curve 2; $pK_A = 4.69$, dashed curve 3. Inset: degree of neutralization, ξ_n , as a function of the base in the dialyzation bath.

10-20%) that occurs in neutral solutions close to pH 7 (i.e., at pH appreciably higher than pK_A due to Donnan equilibrium) promotes intermicellar electrostatic interaction. This observation is understandable: The overall ionization of PMA shells increases, but even though the intrinsic concentration of counterions in the shell is higher than that in the bulk, the overall concentration of the shell-fixed negative charge is still low. The fixed negative charge is insufficient to keep small mobile positive ions in the shell. Some counterions escape into the bulk solvent, and the electrostatic interactions between micelles are not sufficiently screened.

What happens at higher degrees of neutralization (higher than 30%) is somewhat surprising. The concentration of negatively charged -COO⁻ groups fixed on the shell-forming chains increases and electrostatic attraction hinders the escape of counterions into the bulk medium. The pronounced intermicellar electrostatic interactions fade out. However due to Donnan equilibria, the dissociation is strongly suppressed in the inner part of the shell and significant dissociation occurs only in fairly alkaline solutions, where the bulk concentration of ions is quite high. In alkaline solutions (degree of neutralization higher than 80%), the micelles act as neutral objects and polyelectrolyte effects disappear. SLS provide almost regular Zimm plots, and QELS yields a fairly sharp single relaxation mode, proportional to $\sin^2(\theta/2)$ (not shown). The "quasi-neutral behavior" of micelles is first observed in solutions with a concentration of small ions corresponding to the theoretical transition region between the osmotic and salted brush regimes. An excess of base causes the neutralization of almost 100% of acid PMA groups. Small ions (both Na⁺ and OH⁻), which are present at high concentrations, screen electrostatic interactions. The shell behaves as a neutral brush, and both SLS and QELS yield data for almost noninteracting nanoparticles.

To complete the picture of the behavior of micelles in solutions differing in pH, the changes in size of micelles are shown as a function of pH. Figure 7 shows the apparent hydrodynamic radii, $R_{\rm H}$, of large micelles, M2, in dilute salt-free solutions differing in pH (curve 1) and that corresponding to theoretical dependence (curve 2). The main difference, i.e., the shift on the pH scale, is due to the fairly high value of $K_{\rm A}$ (for monomeric



Figure 7. Hydrodynamic radius, $R_{\rm H}$, of micelles M2 in a dilute "salt-free" solution as a function of pH. Concentration of micelles c = 0.05 mg/mL; by the term "salt-free" we mean that only NaOH was added to control pH (curve 1). The simulated $R_{\rm H}$ for p $K_{\rm A} = 4.69$, which corresponds to the dissociation of monomeric methacrylic acid (curve 2).

methacrylic acid) that was used in simulations. Despite nonnegligible differences in absolute values of $R_{\rm H}$, the trends compare well. The curves are similar to those measured and calculated in our earlier studies for similar micellar systems at finite ionic strength.^{5n,18b,c}

Interpretation of Experimental Data with the Help of Computer Simulations and Comparison with Existing Theories and with Experimental Results on Similar Systems. In this part, we compare experimental results with our original MC simulations and with predictions of already existing theories. Furthermore, we put the results of computer simulations into context with the theoretical research already published, and we discuss the advantages, disadvantages and limitations, of our approach. In the end, we compare our experimental data with results of experimental studies on similar systems. Hence, we outline the most important findings both from the experimental and theoretical points of view.

Computer simulations help us to explain important features and trends of the behavior of dilute solutions of polyelectrolyte micelles over a broad region of pH and I. Data on the pH-dependent behavior of solutions of medium ionic strength were published earlier.¹⁸ Here we present only selected data on the behavior of low ionic strength solutions that are necessary for the understanding of the experimental observations. The most important simulation data concern the distribution of positive and negative charges in the shell and in the immediate vicinity of the micelle and the density and ionization profiles of the PMA shell. Parts a and b of Figure 8 show the distribution of charges and the Insert shows the concentration profiles of dissociated $[-COO^{-}]$, nondissociated [-COOH] and all η shell-forming PMA segments, respectively for salt-free solution of micelles at pH 4.9 (close to pK_A of methacrylic acid) for I = 0.001, (inset in a) and 0.1, (inset in b), respectively. Results of simulations show increasing dissociation of -COOH toward the shell periphery and a pronounced effect of the bulk ionic strength on the overall ionization of PMA. For the following detailed discussion of experimental data, we need to analyze the distribution of charges at the micellar periphery and around the micelle. The simulated distribution function for low I shows a broad and diffuse cloud of small positive ions around the



Figure 8. (a) Molar concentration of positively charged small ions (full curve 1) and negatively charged segments (dashed curve 2) in the micellar shell and in the vicinity of the PS-PMA micelle as a function of the distance from the center of the micelle, r, for pH 4.9 and ionic strength, I = 0.001. Inset: Concentration profiles of dissociated, nondissociated, and all PMA segments (i.e., molar concentrations of -COOH groups). (b) The same dependences for pH 4.9 and I = 0.1.

micelle. More precisely, there exists a depletion area of positive ions in the shell and their surplus in the bulk solvent. The region containing the noncompensated charge reaches quite far outside the micelle. Hence, the micelle itself represents an effectively charged nanoobject. The same conclusion may be drawn from the electrostatic potential $\Phi(r)$ as a function of the distance from the micellar center *r* which is significantly negative up to $r \approx 2 R_{\rm g}$ (see Figure 9) for low I = 0.001. Even though we simulate only a single micelle and we are aware of the fact that the distribution of small ions (and the electrostatic intermicellar interaction) will change when two or more micelles come close to each other at elevated concentrations, the simulated charge distribution helps to understand the experimentally observed electrostatic interaction of micelles in dilute solutions with a low ionic strength.

Both the SLS and QELS measurements suggest that the kinetically frozen PS-PMA micelles behave as strongly charged nanoparticles that mutually interact over relatively long distances in pure water and in low ionic strength aqueous solutions. Almost all authors describe frozen polyelectrolyte micelles as inert hydrophobic cores decorated by a dense polyelectrolyte brush. It is therefore interesting to discuss the behavior with respect to that of polyelectrolyte brushes. Planar and convex polymeric brushes represent an important and



Figure 9. Reduced electrostatic potential, i.e., $q_e\phi(r)/kT$, where q_e is the elementary charge, $\phi(r)$ is the electrostatic potential, k is the Boltzmann constant and T is temperature, as a function of the distance from the micellar center, r, for dilute aqueous solution of micelles at pH 4.9 and I = 0.001 and 0.1 (full curve 1' and dashed curve 2', respectively). Curves 1 and 2 show corresponding concentration profiles of PMA in the shell for comparison the range of the electrostatic interaction with the geometric size of micelles.

interesting class of polymer systems and their properties have been the subject of numerous experimental and theoretical studies. Our discussion is based mainly (but not exclusively) on studies of annealed convex brushes formed by weak polyelectrolytes.^{12,29} In our systems, the charges occur as a result of the dissociation of PMA units, and their number and position depend on the bulk pH, ionic strength, and local concentrations of both -COOH and -COO⁻ groups and on local dielectric permittivity, which change with the distance from the core/shell interface. Simple geometric considerations based on comparison of small sizes and the high molar masses of micelles lead to the conclusion that the PMA shell of PS-PMA micelles represents a very densely grafted convex brush. Due, in part, to the spherical symmetry of micelles and to the specific behavior of PMA,²² the density of segments decreases steeply in the periphery of the shell. This region is rather dilute and contains fairly stretched and ionized parts of PMA chains. Both the experimental and simulation results suggest that in pure water, small positive ions do not fully compensate the negative charge of the peripheric PMA layer and try to escape into the bulk for entropy reasons.

Significant changes of the hydrodynamic radius $R_{\rm H}$ of micelles are observed in very dilute solutions of micelles ($c_{\rm P}$ ca. 10^{-1} mg/mL) in the region of very low ionic strength. Traces of NaCl promote dissociation of -COOH groups. An insufficient screening of the electrostatic repulsion between ionized groups at concentrations below 10^{-3} mol/L together with the tendency of trapped counterions to enlarge the volume for their translation motion and to increase entropy causes expansion of micellar shells. At $c_{\rm NaCl}$ ca. 10⁻³ mol/L, a nicely pronounced maximum is reached, and later, the shell starts to shrink (see curve 1 in Figure 10). The observed $R_{\rm H}$ vs I behavior suggests the transition between the "osmotic brush" and "salted brush" regimes, which is well-known,^{12a-c,29f-h} but has been observed very rarely due to experimental difficulties. The behavior of dense quenched brushes may be explained as follows. Because of the high concentration of negative charges (fixed on the polymer chains), small (mostly positive) ions are firmly kept on the osmotic brush at salt concentrations in the bulk solution lower than the



Figure 10. Dependence of the hydrodynamic radius, $R_{\rm H}$, of M2 micelles on p $I = -\log c_{\rm NaCl}$ in aqueous solutions at pH 4.9 in the region of low ionic strengths, I: experimental QELS data (curve 1); simulated data (curve 2).

intrinsic concentration of counterions in the brush, because the electrostatic forces are very strong. They dominate both the elastic forces generated by chain stretching and the "entropic forces" which relax the unfavorable localization of small ions in a small volume. The minimization of the Gibbs function requires local compensation of electric charges in the brush. The brush swells which results in increased entropy of small counterions (osmotic brush). At higher *I*, small ions screen the electrostatic forces and the brush height decreases (salted brush). A comparison of experimental and simulation data is shown in Figure 10. Curve 2 depicts the theoretical $R_{\rm H}$ vs *I* dependence. Both curves are similar.

We would like to point out that the interplay of electrostatic vs osmotic forces and the reasons for the behavior of studied PS-PMA micelles in pure water and in low salt NaCl solutions differ from the abovedescribed model. All experimental and theoretical data show that the shell periphery resembles the Pincus brush more closely than the osmotic brush.

Pincus et al. analyzed the behavior of polyelectrolyte brushes and identified several different regimes of their behavior. $^{29(o,p)}$ Defining a distance scale $\xi,$ over which a test charge is neutralized, he found that for $\xi \ge L$, where L is the brush thickness (this condition corresponds to a low charge density, i.e., to a low ionization degree or low grafting density), the counterions escape into the bulk solution for entropic reasons. The terms "Pincus brush" and "Pincus brush regime" were first used by Israëls et al.^{12a} for the brush, which is effectively strongly charged since it has lost mobile counterions, but the authors concluded that this regime is not practically important and hence this term has not been used in other papers. Some time later, e.g., Borisov and Zhulina^{29g,h} studied a similar system (the polyelectrolyte star with a small ionization degree) under conditions when $Q \ll eR/l_{\rm B}$, where Q is the fixed charge of the star, e the elementary charge, R the radius of the star and $l_{
m B}$ is the Bjerrum length, and they found that a fraction of counterions escapes from the star. They described the behavior as a special case of the osmotic regime not using the term "Pincus brush". In our discussion, we adopted a bit relaxed terminology using terms like "Pincus regime-like behavior" or "the behavior similar to that of the Pincus or osmotic brush" since in experiments (and also in computer experiments), we study

systems where the local charge density and the local charge compensation varies with the distance from the core/shell interface, but our terminology is generally in agreement with that currently used. Nevertheless, we would like to make a brief comment explaining our description of shell regimes: experimental data⁵ show that in PS-PMA micellar aqueous solutions, different parts of the shell (the inner and the peripheric) obey sometimes different regimes, because the density and the ionization degree of PMA change considerably across the shell. We take this fact into account in the discussion of both experimental and simulation data.

The conclusions concerning the behavior of micelles in solutions at extremely low ionic strength agree with the results of theoretical calculations and compare well with observations at higher concentrations (even though any simple and straightforward extrapolation of the conclusions made on the interaction of a single micelle with the cloud of counterions to more concentrated micellar solutions is impossible): when the average distances of closest pairs of micelles are two to three times larger than their hydrodynamic diameter, strong electrostatic interactions between electrically noncompensated micelles and a common cloud of free counterions in the solution dominate the solution behavior and influence light scattering data.

The experimental dependence of $R_{\rm H}$ on I depicted in curve 1 was measured at very low micellar concentrations (ca. 0.1 g/L), at which the average closest distance between micelles is large and interactions between micelles do not play important role. A similar curve going through a maximum was observed also at higher micellar concentrations. In this case, both the apparent hydrodynamic radii $R_{\rm H}^{\rm ap}$ and the position of the maximum were shifted to different values because the measurement was strongly affected by electrostatic interactions and by correlation effects.

The micellar solutions with partly neutralized PMA shells show very interesting behavior. The concentration of ionized $-COO^-$ groups in the outermost layer of the shell increases upon addition of the base and the electrostatic forces keep a fraction of positively charged counterions in the shell. The Pincus-brush-like behavior of the shell changes partially in favor of the osmotic-brush-like regime and micelles behave as noncharged objects.

In this paper, we use results of our own simulations for practical reasons. The same type of "coarse-graining" and "back-mapping" procedure for micelles studied in nonaqueous^{18a} and in aqueous media^{18c} (and this work) allows for a reasonable quantitative comparison of experimental and simulated sizes of micelles. Even more important is the fact that from the experimental point of view, it is much easier to measure pH than to evaluate accurately the degree of dissociation. In our earlier papers,⁵ we have shown that the alkalimetric titration is difficult for PS-PMA systems and in this study we demonstrated that the time-consuming dialysation procedure should be used for an accurate evaluation of the degree of neutralization. Hence our MC simulations, which use bulk pH and bulk ionic strength as independent parameters, are better suited for the analysis of the observed experimental trends than theories that assume the degree of dissociation.

In the next part, we compare our results (both experimental and computer-based) with the already existing theories and experiments. As mentioned above,

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annealed polymer brushes (both planar and curved) has been a subject of numerous theoretical studies.²⁹ The most advanced and the most recognized are the scaling theories developed by Borisov and Zhulina^{12b,c,29} g⁻¹ (in cooperation with few other authors) and their combinations with self-consistent-field numerical calculations developed by the Waageningen group.^{12a,c,29m,n} These theories are at present able to describe all decisive features of annealed convex brushes, including micellar shells.

We would like to point out that our results agree at the semiquantitative level with all decisive general trends predicted by the existing scaling concepts. In MC simulations, the shell forming chains are fairly short, and therefore, we find some differences in comparison with theories (which assume infinitely long chains). A careful snapshot analysis (based on ca. 10² chain conformations) reveals that short chains do not form blobs and simulations also underestimate the scaling exponents. However our theoretical modeling was not aimed at the scaling laws. We were interested in the distribution of ions and in the shell density and ionization profiles. For a better understanding and discussion of our experimental data and the effects of electrostatic interactions, we developed an alternative computerbased method for the study of charged spherical nanoparticles. This method proved to be useful and may be used not only for regular micelles but also for the hydrophobically modified (e.g., fluorescently tagged micelles or micelles with only partially hydrolyzed shellforming blocks). Besides the already mentioned practical reasons, another advantage of MC simulations consists of the fact that no a priori assumptions on the blob structure and distribution of fixed ions and counterions are necessary for computer experiments. Monte Carlo simulations belong to the category of pseudo-experimental methods, and their results compare well with our SCF calculations,^{18b} but in contrast to SCF, they provide detailed information on conformations of individual shell-forming chains, which is, e.g., necessary for the interpretation of fluorescence data (e.g., nonradiative energy transfer) on labeled micelles.^{5k,1} For a proper understanding of our experimental observations, it is important that simulations yield detailed information on the shell density and dissociation profiles and on the distribution of small ions.

The most severe drawback of our technique lies in the fact that we study a single micelle immersed in the solution. As concerns the changes of micellar sizes in very dilute solutions, the simulation yields results, which are plausible and suitable for comparison with experimental data. However, all considerations concerning intermicellar interactions at finite concentrations have to be regarded as an indirect support of conclusions drawn from the experimental study only, and it is why we have been very careful not to do any speculative deductions. We just want to point out that, under certain conditions, the counterions do not locally screen the micellar charge and the electrostatic potential is nonzero at fairly long distances from the micellar center (comparable with the micellar radius). Hence the micelles sharing a common cloud of counterions may mutually interact electrostatically at higher concentrations, which we do observe by light scattering. Another disadvantage of simulations is a relatively long CPU time necessary for reliable simulations along with the generally recognized fact that results of simulations

represent a collection of isolated computer experiments and a large series of data has to be gathered to trace unambiguously all trends of the behavior. The last important disadvantage of MC is the necessity to reduce the complexity of the system and to use relatively short chains for practical reasons.

Since the space distribution of counterions in micelles with shells formed by a strong polyelectrolyte, poly-(styrene-sulfonate), has been already studied by Monte Carlo simulations³⁰ we want to compare the results for the high ionization limit. The authors used a very simplified model, in which the shell-forming chains were replaced by rigid linear rods oriented in the radial direction with constant charge spacing. They found three types of small ions. Inside the brush, some ions are firmly bound to the negatively charged rods and the other are relatively free and can move in the brush, but they do not escape in the bulk solvent. These two types represent the overwhelming majority of all ions in the system. At the outermost periphery, there exists the electrical double layer since a small amount of ions escape in the solution and stay close to the charged nanoobject. The thickness of the double layer is very small as compared with the thickness of the brush. The simulation corresponds to micelles with rigid and fully ionized soluble chains. The distribution of small ions (which are mostly trapped in the shell) explains the almost negligible electrostatic interaction of micelles with strong polyelectrolyte shells at distances appreciably larger than the thickness of the double layer. Our simulation is less simplified since it assumes flexible chain conformations, but as concerns the charge distribution in the high ionization limit, our results for PS-PMA micelles agree with the reported behavior.

Among numerous experimental studies of watersoluble micelles, the polyelectrolyte behavior and size changes of micelles with shells formed by weak polyelectrolytes in medium and high ionic strength solutions represent an intensely studied topic since many micellar systems are very stable in salted solutions and the stability is the key issue for their potential applications. We studied the size changes and polyelectrolyte behavior of PMA and PVP shells in solutions differing in pH and *I* in a couple of our earlier papers.⁵ Size changes of micelles, shell density profiles, and distribution of ions and their dependences on the degree of ionization and the concentration were studied by many other groups, e.g., by Förster,^{31a,b} van der Maarel,^{31c,d} Harihanan,^{29e} Lee,^{31e} and Wesley.^{31f} Although we do not study salted micellar solutions in this paper, the last two articles (both from the University of Sussex) are very interesting and worth discussing. The authors of both papers compare their data with scaling and SCF theories and Wesley et al.^{31f} studied also the polyelectrolyte behavior of micelles at fairly low ionic strength. Lee et al.^{31e} studied similar dependencies as we did recently in our paper on the computer simulation methodology,^{18c} but the studied system was very complex and a direct comparison is difficult. They studied several pHresponsive copolymers formed by two blocks, which do not differ much in polarity. The core-forming block is even soluble at certain temperatures and in a certain pH region. At a critical pH, the core-forming block becomes insoluble and reversible micelles are formed. Since the core is not frozen, not only the state (size and ionization) of the shell but also the association number and the compactness of the core depend on pH and I. The measured dependences are complex and reflect the combination of several effects. The authors prepared several diblocks with ionized and neutral shells and by using a fairly sophisticated attitude they were able to separate individual contributions. They report that their experimental results compare well with predictions of the scaling theories by Zhulina et al.^{29g,h} and conclude that the ionized shell may be described by the electrostatic blob picture. Our already published data^{18c} show trends that agree qualitatively with individual separated contributions reported by Lee et al,^{31e} but the simulated log–log $R_{\rm H}$ vs $\xi_{\rm n}$ and $c_{\rm salt}$ dependences are weaker, which is due to relatively short chains used in simulations.

To our knowledge, nobody studied experimentally the behavior and size changes of micelles at extremely low ionic strengths, which would have required avoiding the contamination by alkaline ions from glass vessels and (especially for weak polyacids) the contamination by CO₂ (and hence working in N₂ atmosphere). We are aware of only one experimental work in this respect, even though the experimental conditions were not so strictly controlled. A similar dependence of $R_{\rm H}$ on ionic strength going through a maximum (an analogous curve to that shown in Figure 10) was reported by Wesley et al.^{31f} for poly(methyl methacrylate)-block-poly(2-(dimethylamino)methacrylate brushes grafted to polystyrene latex particles, but the curve $R_{\rm H}^{\rm app}$ vs I was measured in solutions with a relatively high concentration of nanoparticles and hence the values could have been affected by electrostatic interactions, which, as we have shown experimentally, are fairly strong in low ionic strength solutions and influence the behavior and light scattering data.

Remarks on the Specific Behavior of the PMA Shell. Poly(methacrylic acid) belongs to the most studied polyelectrolytes. Its atypical behavior attracted attention first in fifties and 1960s of the last century, but the studies continue until now.²² It was shown a fairly long time ago, e.g., by Katchalski,^{22a} Morawetz,^{22g} and Ghiggino^{22f} and by others that PMA is not a typical polyelectrolyte but has some properties of polysoaps. Because of the presence of the strongly hydrophobic methyl group in each repeating unit, it is not very soluble at low pH and adopts a very compact globular form. Ghiggino actually proposed a sort of "necklace of pearls" structure in 1985 on the basis of indirect fluorescence studies. It was pointed out by Morawetz^{22g} and by Bednář^{22h} that the changes in solubility with pH are not caused by the appearance of the electrical charge after dissociation only, but significant changes in the solvation and in the structure of solvating water occur. Using fluorescence measurements, both authors also concluded that the collapsed domains are fairly hydrophobic.

We have been studying the structure and properties of PMA shells for a fairly long time experimentally (mainly by a combination of light scattering and fluorescence techniques).⁵ On the basis of fluorescence studies, we concluded that the shell consists of a fairly hydrophobic dense inner layer, which is formed by collapsed nondisociated PMA (this layer is able to solubilize nonpolar molecules) and a diluted peripheric layer formed by ionized and fairy stretched ends of PMA chains, preferentially oriented in the radial direction. Our indirect conclusions were later confirmed by neuScheme 1. Changes in the Structure and Ionization of Micelles and Changes in the Spatial Distribution of Small Ions around Micelles with pH and I of the Bulk Solution



tron scattering studies aimed at the shell density profile. $^{\rm 31a,b}$

The specific behavior of PMA was not taken into account in simulation. We modeled PMA in water as a polyelectrolyte in bad solvent, but possible differences in the behavior due to different solvation of dissociated and nondissociated units (which could have been reflected by different interaction parameters) were neglected. The consideration and inclusion of specific interactions of PMA with water could explain significant differences between the solution behavior of poly-(methacrylic acid) and poly(acrylic acid), including the differences in effective pK_A vs degree of dissociation, but unfortunately there is not enough information at present. Therefore, we expect that simulations slightly underestimate the differences in properties of the inner and peripheric PMA shell as compared with real PS-PMA micelles in water.

Conclusions

The kinetically frozen multimolecular block polyelectrolyte PS-PMA micelles were studied by a combination of several experimental techniques in low ionic strength aqueous solutions. All methods used show that, at low I, the micelles behave as considerably charged nanoparticles, i.e., as nanoobjects with noncompensated electric charges that interact with each other over relatively long distances in salt-free and in low-salt-content solutions. Computer studies combining mechanistic Monte Carlo simulations for systems of tethered self-avoiding chains with the solution of the Poisson-Boltzmann equation for the evaluation of the electrostatic contribution were performed. Results of computer studies compare fairly well with existing scaling theories and selfconsistent-field studies and provide deeper insight into the behavior of PMA shells.

All data confirm that the outermost part of the PMA shell is fairly dissociated. The unscreened electrostatic forces act at fairly long distances and dominate the solution behavior at low ionic strength. Strong intermicellar interactions and correlations affect light scattering from aqueous solutions of PS-PMA micelles. The PMA shell basically behaves as a convex annealed polyeletrolyte brush, but its ionized periphery resembles more the Pincus brush than the osmotic brush at low bulk ionic strength. During neutralization, the concentration of fixed negatively charged carboxylic groups in the shell increases with the addition of base. Strong electrostatic interactions hinder the escape of positively

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charged counterions from the shell and the pronounced polyelectrolyte behavior corresponding to the Pincusbrush-like regime partially diminishes and changes in favor of the osmotic-brush-like regime, before the shell starts to behave as the salted brush. The main changes in the shell structure, in PMA dissociation and in the distribution of small ions around the micelles with pH and I are depicted in Scheme 1.

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References and Notes

- (a) Webber, S. E., Munk, P., Tuzar, Z., Eds. Solvents and Selforganization of Polymers; NATO ASI Series E, Vol. 327. Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996. (b) Hamley I. W. Physics of Block Copolymers; Oxford University Press: Oxford, England, 1998.
- (2) (a) Tuzar, Z.; Kratochvíl, P. In Surface and Colloid Science; Matijevic, E., Ed.; Plenum Press: New York, 1993; Vol. 15, p 1.
- (3) (a) Tuzar, Z.; Webber, S. E.; Ramireddy, C.; Munk, P. Polym. Prepr. 1991, 32 (1), 525. (b) Tian, M.; Quin, A.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z.; Procházka, K. Langmuir 1993, 9, 1741. (c) Kiserow, D.; Procházka, K.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. Macromolecules 1992, 25, 461.
- (4) Thurmond, K. B.; Kowalewski, T.; Wooley, K. L. J. Am. Chem. Soc. 1997, 119, 6656.
- (5)(a) Procházka, K.; Kiserow, D.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. Macromolecules 1992, 25, 454. (b) Ramireddy, C.; Tuzar, Z.; Procházka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992**, *25*, 2541. (c) Tsitsilianis, C.; Voulgaris, D.; Štěpánek, M.; Podhájecká, K.; Procházka, K.; Tuzar, Z.; Brown, W. Langmuir 2000, 16, 6868. (d) Martin, T. J.; Procházka, K.; Munk, P.; Webber, S. E. Macromolecules 1996, 29, 6518. (e) Procházka, K.; Martin, T. J.; Webber, S. E.; Munk, P. Macromolecules 1996, 29, 6526. (f) Štěpánek, M.; Procházka, K. Langmuir 1999, 15, 8800. (g) Štěpánek, M.; Procházka, K.; Brown, W. *Langmuir* **2000**, *16*, 2502. (h) Pleštil, J.; Kříž J.; Tuzar, Z.; Procházka, K.; Melnichenko, Yu, B.; Wignall, G. D. Talingting, M. R.; Munk, P.; Webber, S. E. Macromol. Chem. Phys. 2001, 202, 553. (i) Stěpánek, M.; Podhájecká, K.; Tesařová, E.; Procházka, K.; Tuzar, Z.; Brown, W. *Langmuir* **2001**, *17*, 4240. (j) Podhájecká, K.; Štěpánek, M.; Procházka, K.; Brown, W. *Langmuir* **2001**, *17*, 4245. (k) Matějíček, P.; Uhlík, F.; Limpouchová, Z.; Procházka, K.; Tuzar, Z.; Webber, S. E. Macromolecules 2002, 35, 9487. (l) Matějiček, P.; Humpolíčková, J.; Procházka, K.; Tuzar, Z.; Špírková, M.; Hof, M. Webber, S. E. J. Phys. Chem. B 2003, 107, 8232. (m) Humpolíčková, J.; Procházka, K.; Hof, M.; Tuzar, Z.; Špírková, M. Langmuir 2003, 19, 4111. (n) Karymov, M. A.; Procházka, K.; Mendenhall, J. M.; Martin, T. J.; Munk, P.; Webber, S. E. *Langmuir* **1996**, *12*, 4748. (o) Munk, P.; Tuzar, Z.; Procházka, K. Collect. Czech. Chem. Commun. 1997, 62, 1738. (p) Talingting, M. R.; Munk, P.;
 Webber, S. E.; Tuzar, Z. Macromolecules 1999, 32, 1593. (q) Tian, M.; Arca, E.; Tuzar, Z.; Webber, S. E.; Munk, P. J. Polym. Sci., Polym. Phys. **1995**, 33, 1713. (r) Qin, A.; Tian, M.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z. Macromolecules 1994 27, 120.
- (6) (a) Wilhelm, M.; Zhao, C.-L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J.-L.; Riess, G.; Croucher, M. D. Macromolecules 1991, 24, 1033. (b) Rager, T.; Meyer, W. H.; Wegner, G.; Winnik, M. A. Macromolecules 1997, 30, 4911. (c) Astafieva, I.; Zhong, X. F.; Eisenberg, A. Macromolecules 1993, 26, 7339. (d) Astafieva, I.; Khougaz, K.; Eisenberg, A. Macromolecules

1995, 28, 7127. (e) Yu, Y. S.; Zhang, L. F.; Eisenberg, A. Langmuir **1997**, 13, 2578. (f) Zhang, L. F.; Eisenberg, A. Macromolecules **1999**, 32, 2239. (g) Shen, H. W.; Zhang, L. F.; Eisenberg, A. J. Am. Chem. Soc. **1999**, 121, 2728. (h) Shen, H. W.; Eisenberg, A. J. Phys. Chem. B **1999**, 103, 9473. (i) Shen, W. H.; Eisenberg, A. Macromolecules **2000**, 33, 2561.

- (7) (a) Butun, V.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. J. Am. Chem. Soc. 1999, 121, 4288. (b) Lee, A. S.; Gast, A. P.; Butun, V.; Armes, S. P. Macromolecules 1999, 32, 4302.
- (8) (a) Booth, C.; Yu, G.-E.; Nace, V. M. Block copolymers of ethylene oxide and 1,2-butylene oxide. In Amphiphilic block copolymers: self-assembly and applications; Alexandrids, P., Lindman, B., Eds.; Elsevier: Amsterodam, 1997. (b) Wilhelm, M.; Zhao, C.-L.; Wang, Y.; Xu, R.; Winnik, M. A.; Mura, J.-L.; Riess, G.; Croucher, M. D. Macromolecules 1991, 24, 1033. (c) Brown, W.; Schillen, K.; Almgren, M.; Hvidt, V.; Bahadur, P. J. Phys. Chem. 1991, 95, 1850. (d) Mortensen, K.; Pedersen, J. S. Macromolecules 1993, 26, 805. (e) Wu, G. W.; Chu, B. Macromolecules 1994, 27, 1766. (f) Linse, P. Macromolecules 1994, 27, 6404. (g) Alexandridis, S.; Hatton, T. A. Colloids Surf. A 1995, 10, 1. (h) Mortensen, K. Polym. Adv. Technol. 2001, 12, 2. (i) Perreur, C.; Habas, J. P.; Francois, J.; Peyrelasse, J.; Lapp, A. Phys. Rev. E. 2002, 65, Art. No. 041802, Part 1. (j) Park, M. J.; Char, K.; Kim, H. D.; Lee, C. H.; Seong, B. S.; Han, Y. S. Macromol Res. 2002, 10, 325.
- (9) Wooley, K. L. J. Polym. Sci., Polym. Chem. 2000, 38, 1397.
- (10) (a) Antonietti, M.; Förster, S.; Östreich, S. Macromol. Symp. 1997, 121, 75. (b) Regenbrecht, M.; Akari, S.; Förster, S.; Mohwald, H. J. Phys. Chem. B 1999, 103, 6669. (c) Erhardt, R.; Boker, A.; Zettl, H.; Kaya, H.; Pyckhout-Hintzen, W.; Krausch, G.; Abetz, V.; Mueller, A. H. E. Macromolecules 2001, 34, 1069.
- (11) Förster, S.; Hermsdorf, N.; Böttcher, C.; Lindner, P. Macromolecules 2002, 35, 4096.
- (12) (a) Israels, R.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B. Macromolecules 1994, 27, 3249. (b) Borisov, O. V.; Zhulina, E. B.; Birshtein, T. M. Macromolecules 1994, 2, 7, 4795. (c) Lyatskaya, Yu. V.; Leermakers, F. M. A.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. Macromolecules 1995, 28, 3562. (d) Shusharina, N. P.; Nyrkova, I. A.; Khokhlov, A. R. Macromolecules 1996, 29, 3167. (e) Shusharina, N. P.; Linse, P.; Khokhlov, A. R. Macromolecules 2000, 33, 3829. (f) Misra, S.; Mattice, W. L.; Napper, D. H. Macromolecules 1994, 27, 7090.
- (13) Berne, B. J.; Pecora, R. Dynamic Light Scattering, J. Wiley-Interscience: New York, 1976.
- (14) Jakeš, J. Czech. J. Phys. 1988, B38, 1305.
- (15) Kratochvíl, P. In Classical Light Scattering from Polymer Solutions, Polymer Science Library 5; Jennkins, A. D., Ed.; Elsevier: Amsterdam, 1987.
- (16) Tuzar, Z.; Kratochvíl, P. Collect. Czech. Chem. Commun. 1967, 32, 3358.
- (17) (a) Thompson, N. L. In Topics in Fluorescence Spectroscopy; Lakowicz, J. R., Ed.; Plenum Press: New York, 1991; Vol. 5.
 (b) Webb, W. E. In Fluorescence Correlation Spectroscopy. Theory and Applications; Riedler, R., Elson, E. S., Eds.; Springer-Verlag: Berlin, 2001. (c) Hink, M. A.; van Hoek, A.; Visser, A. J. W. G. Langmuir 1999, 15, 992. (d) Meseth, U.; Wohland, T.; Rigler, R.; Vogel, H. Biophys. J. 1999, 76, 1619.
- (18) (a) Uhlík, F.; Limpouchová, Z.; Jelínek, K.; Procházka, K. J. *Chem. Phys.* 2003, *118*, 11258. (b) Jelínek, K.; Uhlík, F.; Limpouchová, Z.; Procházka, K. J. *Phys. Chem. B* 2003, *107*, 8241. (c) Uhlík, F.; Jelínek, K.; Limpouchová, Z.; Procházka, K. J. Chem. Phys. 2004, *121*, 2367.
- (19) (a) Siepmann, J. I.; Frenkel, D. Mol. Phys. 1992, 75, 59. (b) Rosenbluth, M. N.; Rosenbluth, A. W. J. Chem. Phys. 1955, 23, 356.
- (20) Limpouchová, Z.; Procházka, K. Macromol. Theory Simul. 2004, 13, 328.
- (21) Metropolis, N.; Rosenbluth, M. N.; Rosenbluth, A. W.; Teller, H. J. Chem. Phys. **1953**, 21, 1087.
- (22) (a) Katchalski, A. J. Polym. Sci. 1951, 7, 393. (b) Arnold, R. J. Colloid Sci. 1957, 1, 549. (c) Anufrieva, E. V.; Birshtein, T. M.; Nekrasova, T. N.; Ptitsyn, C. B.; Scheveleva, T. V. J. Polym. Sci., Part C 1968, 16, 3519. (d) Delben, F.; Crezcenzi, V.; Quadrifoglio, F. Eur. Polym. J. 1972, 8, 933. (e) Koenig, J. L.; Angood, A. C.; Semen, J.; Lando, J. B. J. Am. Chem. Soc. 1969, 91, 7250. (f) Ghiggino, K. P.; Tan, K. L. In Polymer Photophysics; Phillips, D., Ed.; Chapman and Hall: London, 1985; Chapter 7. (g) Wang, Y. C.; Morawetz, H. Macromolecules 1986, 19, 1925. (h) Bednář, B.; Trněná, J.; Svoboda,

P.; Vajda, Š.; Fidler, V.; Procházka, K. *Macromolecules* **1991**, 24, 2054. (i) Soutar, I.; Swanson, L. *Macromolecules* **1994**, 27, 4304.

- (23) Hounter, R. J. Foundation of colloid science; Oxford Science Publications: Oxford, England, 1995; Vol. 1, p 331.
- (24) (a) Morcellet, M.; Wozniak, M. *Macromolecules* 1991, 24, 745.
 (b) Porasso, R. D.; Benegas, J. C.; van den Hoop, M. A. G. T. J. Phys. Chem. B 1999, 103, 2361.
- (25) Lide, D. R., Frederikse, H. P. R. Eds.; Handbook of Chemistry and Physics, 76th ed.; CRC Press: Boca Raton, FL, 1995.
- (26) Brandrup, J., Immergut, E. H., Eds. *Polymer Handbook*, 2nd ed; J. Wiley Interscience: New York, 1975.
- (27) (a) Pusey, P. N. Introduction to Scattering Experiments. In Lindner, P., Zemb, T., Eds.; Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter; Elsevier: Amsterdam, 2002; p 3 Pusey, P. N. Dynamic Light Scattering. In Lindner, P., Zemb, T., Eds.; Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter; Elsevier: Amsterdam, 2002; p 203. (b) Sedlák M. Polyelectrolytes in solution. In Brown W., Ed. Light Scattering. Developments and Principles; Clarendon Press: Oxford, England, 1996; p 120. Schurtenberger, P. Light Scattertering. Developments and Principles; Clarendon Press: Oxford, England, 1996; p 293.
- (28) Gröhn, F.; Antonietti, M. Macromolecules 2000, 33, 5938.
- (29) (a) Balazs, A. C.; Singh, C.; Zhulina, E.; Chern, S.-S.; Lyatskaya, Y.; Pickett, G. Prog. Surf. Sci. 1997, 55, 181. (b) Tran, Y.; Auroy, P.; Lee, L.-T. Macromolecules 1999, 32, 8952. (c) Ahrens, H.; Förster, S.; Helm, C. A. Macromolecules 1997, 30, 8447. (d) Hariharan, R.; Biver, C.; Russel, W. B. Macromolecules 1998, 31, 7514. (e) Hariharan, R.; Biver, C.; Mays,

J.; Russel, W. B. Macromolecules 1998, 31, 7506. (f) Balastre,
M.; Li, F.; Schorr, P.; Yang, J. C.; Mays, J. W.; Tirrel, M. V.
Macromolecules 2002, 35, 9480. (g) Borisov, O. V.; Zhulina,
E. B. Eur. Phys. J. B 1998, 4, 205. (h) Zhulina, E. B.; Borisov,
O. V. Macromolecules 2002, 35, 9191. (i) Borisov, O. V.;
Zhulina, E. B. Macromolecules 2003, 36, 10029. (j) Zhulina,
E. B.; Borisov, O. V.; Birshtein, T. M. Macromolecules 1999, 32, 8189. (k) Zhulina, E. B.; Borisov, O. V. Macromolecules 1995, 28, 1491. (m) Wolterink, J. K.;
Leermakers, F. A. M.; Fleer, G. J.; Koopal, L. K.; Zhulina, E. B.; Borisov, O. V. Macromolecules 1999, 32, 2365. (n) Currie,
E. P.; Sieval, A. B.; Fleer G. J.; Cohen Stuart, M. A. Langmuir 2000, 16, 8324. (o) Pincus, P. Macromolecules 1991, 24, 2912. (p) Ross, R. S.; Pincus. P. Macromolecules 1992, 25, 1503.

- (30) (a) Roger, M.; Guenoun, P.; Muller, F.; Belloni, L.; Delsanti, M. *Eur. Phys. J.* **2002**, *9*, 313. (b) Belloni, L.; Delsanti, M.; Fontaine, P.; Muller, F.; Guenoun, P.; Mays, J. W.; Boesecke, P.; Alba, M. *J. Chem. Phys.* **2003**, *119*, 7560.
- (31) (a) Förster, S.; Hersmdorf, N.; Bottcher, C.; Lindner, P. Macromolecules 2002, 35, 4096. (b) Förster, S.; Abetz, V.; Müller A. H. E. Adv. Polym. Sci. 2004, 166, 173. (c) Groenewegen, W.; Egelhaaf, S. U.; Lapp, A.; van der Maarel, J. R. C. Macromolecules 2000, 33, 3283. (d) Groenewegen, W.; Lapp, A.; Egelhaaf, S. U.; van der Maarel, J. R. C. Macromolecules 2000, 33, 4080. (e) Lee, A. S.; Butun, V.; Vamvakaki, M.; Armes, S. P.; Pople, J. A.; Gast, A. P. Macromolecules 2002, 35, 8540 (f) Wesley, R. D.; Cosgrove, T.; Thompson, L.; Armes, S. P.; Billingham, N. C.; Baines, F. L. Langmuir 2000, 16, 4467.

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