Soluble Complexes of Sodium Poly(isoprene-*b*-methacrylate) Micelles with Cationic Surfactants in Aqueous Media

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Water-soluble complexes between sodium poly(isoprene-*b*-methacrylate) (NaIMA) amphiphilic block copolymer micelles and two cationic surfactants with different hydrophobic tail lengths, namely, dodecyltrimethylammonium bromide (DTMAB) and octyltrimethylammonium bromide (OTMAB), were prepared by mixing individual aqueous solutions of block copolymers and surfactants. The complexes were characterized in terms of size, overall charge, and micropolarity by dynamic light scattering, ζ-potential measurements, and fluorescence spectroscopy. Properties of the systems were investigated as a function of surfactant concentration and surfactant type and state in the initial solutions, as well as temperature. Experiments reveal surfactant complexation at the coronal sodium poly(methacrylate) (NaMA) chains, followed by an increase in mass and a decrease in size of the micelles. Complexation of individual surfactant micelles was observed when the DTMAB concentration in the starting solutions was higher than the surfactant cmc. The complexes show a temperature dependence of their dimension due to the hydrophobic effect.

Introduction

Amphiphilic block copolymers constitute a very active field of research in recent years. The interest in these macromolecules stems from their ability to form a variety of self-assembled nanostructures in aqueous solutions, which in turn have a great potential for practical applications, including drug delivery systems, environmental purification methodologies, cosmetic and detergent formulations, agricultural adjutants, and nanoreactors and nanotemplates for catalysis and nanostructural materials preparation.[1–3]

In parallel, the interaction of amphiphilic block copolymer nanostructures with low molecular weight surfactants has also received considerable attention,[4–6] since in many technical applications amphiphilic block copolymers are used together with surfactants. The academic interest on mixed block copolymer/surfactant systems in the past few years has been focused mainly on the interaction of double-hydrophilic block copolymers, containing an ionic and a nonionic water-soluble block, in which amphiphilicity can be induced by changes in a variety of system parameters (pH, ionic strength, temperature, surfactants), with oppositely charged surfactants.[7–12] Triblock copolymer/surfactant systems with copolymers having a hydrophobic block, a charged block, and a nonionic block have also been investigated to a lesser extend.[13,14] However, works on soluble hydrophobic–ionic block copolymer systems with oppositely charged surfactants in aqueous solutions are scarce.[15–17] The main reason must be the fact that mostly insoluble complexes are formed in this case. Due to neutralization of the ionic corona by surfactant binding, the complexes are insoluble in aqueous media but can be soluble in organic media.[18–21] Nevertheless, such systems are interesting since new possible nanostructures can be envisioned in aqueous solutions, extending the already observed ones and widening the knowledge on mixed amphiphilic block copolymer/surfactant solutions. Additionally, some analogies to surfactant binding on polyelectrolyte brushes exist since the micellar corona can be regarded as a spherical brush.[22]

In this paper the preparation of water-soluble, nonstoichiometric, complexes formed between amphiphilic block copolymer micelles of sodium poly(isoprene-*b*-methacrylate) (NaIMA) and two cationic surfactants, dodecyltrimethylammonium bromide (DTMAB) and octyltrimethylammonium bromide (OTMAB), is reported. The properties of the systems are investigated by dynamic light scattering, ζ-potential measurements, and fluorescence spectroscopy as a function of the preparation protocol, length of the surfactant tail, surfactant concentration, and temperature. The observed behavior of these novel self-assembled systems is discussed taking into account effects related to surfactant binding on the anionic corona of the block copolymer micelles. Such systematic study has not been reported so far to the best of my knowledge, and the present results show some rather unexpected behavior regarding the influence of the preparation protocol, the effects of the surfactant tail length, and the temperature.

Experimental Section

Polymer Synthesis. The diblock copolymer precursor containing polyisoprene (PI) with high 1,4 microstructure and *tert*-butylmethacrylate (PBMA) blocks was synthesized by anionic polymerization high-vacuum techniques,[23] following a procedure similar to the preparation of poly(butadiene-*b*-*tert*-butylmethacrylate) diblocks.[24] Isoprene monomer was first polymerized in benzene using *s*-BuLi as the initiator, and a sample was withdrawn for molecular characterization of the polyisoprene block after completion of the polymerization (ca. 24 h). The active PILi solution was transferred into an ampule equipped with a break seal. This ampule was attached to a second polymerization reactor containing THF, in 2.5-times volume excess over the volume of the PILi solution in benzene. To this reactor were also attached ampules containing purified diphenylethylene (DPE) in hexane (in 3-times molar excess over

the living ends), LiCl in THF (5-times molar excess over the living ends), and purified *tert*-butylmethacrylate (*t*-BMA) monomer. The reactor was immersed into a dry ice/2-propanol bath at −78 °C, and DPE, LiCl, and PILi were introduced by that order under stirring, by breaking the appropriate break seals. Following the capping reaction between PILi and DPE (ca. 15 min), *t*-BMA was introduced into the reactor by distillation from its ampule and allowed to polymerize for 4 h. The polymerization was finally terminated with degassed methanol. The copolymer was precipitated in methanol, containing 20 vol % distilled water, and stabilized with 2,6-di-*tert*-butyl-*p*-cresol. The sample was thoroughly dried in a vacuum oven for a period of 1 week or more.

The amphiphilic poly(isoprene-*b*-sodium methacrylate) diblock was synthesized by hydrolysis of the PB−PtBMA block copolymers and subsequent neutralization of the COOH groups with NaOH. Block copolymer samples were dissolved in distilled dioxane to which a stoichiometric excess of HCl over the ester groups was added.[24,25] 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 N_2 flow, to prevent side reactions on the PI block at the temperature of the reaction. The reaction was allowed to proceed for 6 h. The solution was decanted in acetone, and the solid modified copolymer was washed repeatedly with acetone and dried in a vacuum oven.

The dry poly(isoprene-*b*-methacrylic acid) (PI−PMMA) block copolymer was dissolved in THF (about 2 wt % solution), and the calculated stoichiometric amount of NaOH for complete neutralization of the COOH groups was added, as an ethanolic solution, dropwise through a volumetric pipet under vigorous stirring. Stirring was continued for 1 h after completion of the NaOH addition to ensure complete neutralization of the COOH groups. At the end of the neutralization process THF and ethanol were removed partially in a rotory evaporator, and the inhomogeneous solution was decanted in acetone. The solid copolymer was recovered and dried under vacuum. It was then dissolved in distilled water and subjected to exhaustive dialysis, using Spectra/Por 7 dialysis membranes with a nominal molecular weight cutoff of 3500, from Spectrum Laboratories Inc., until the conductivity of the dialyzate reached that of the water used (<1.9 μS/cm). The copolymer was isolated by freeze-drying and used for the preparation of aqueous solutions. The sample was denoted as NaIMA-1.

Solution Preparation. Stock solutions of NaIMA-1 were prepared by dissolving a weighed amount of the dialyzed sample in the appropriate volume of distilled water (conductivity <1.9 μS/cm), filtered through 0.45 μm hydrophilic Teflon Millipore filters, by heating at 60 °C overnight to facilitate complete dissolution of the copolymer. Solutions of lower concentrations were prepared by dilution of these solutions. Concentrations in the range of 1×10^{-4} to 5×10^{-4} g/mL were utilized. All solutions had the characteristic bluish tint related to the presence of block copolymer micelles.

Dodecyltrimethylammonium bromide (DTMAB) and octyltrimethylammonium bromide (OTMAB), from Aldrich, were used as received. The surfactants were dissolved in distilled water in order to give solutions of the desired starting concentration. Mixed solutions of the block copolymer and the surfactants were prepared by adding different volumes of the surfactant solution (dropwise under stirring, using a buret and at a rate of approximately 2 drops/min) to the same volume of block copolymer solutions and by adding water to a final fixed volume (approximately 15 mL). In this way solutions having

the same copolymer concentration, but different surfactant concentrations, were prepared. The solutions were allowed to stand overnight for equilibration. In the first series of solutions (protocol A) surfactant concentrations in the initial solutions added were kept below the surfactant cmc. For DTMAB, mixed solutions with final surfactant concentrations below the cmc were also prepared, starting from initial solutions containing surfactant micelles (protocol B), to investigate the effect of the surfactant state in the initial solution (nonaggregated or in micellar form) on the characteristics of the resulting complexes. Since it is not possible to achieve the same mixing ratios in both protocols, without exceeding surfactant cmc in the initial solution in protocol A, different surfactant concentration ranges were investigated in the two protocols. The solution's pH was found to be in the range of 6.8−7.6 in all cases; therefore, close to 100% dissociation of the carboxylic groups is expected.[11] The aforementioned solution preparation protocols resulted in micellar solutions that were stable against precipitation for several months. Before light scattering and ζ-potential measurements all solutions were filtered through 0.45 μm hydrophilic Teflon filters (Millex-LCR) obtained from Millipore. Measurements were performed after 24 h of solution preparation. Experiments performed after a week and several months later showed no change (within experimental error) in the properties measured.

For fluorescence measurements pyrene (Aldrich, recrystallized from ethyl acetate) was used as a hydrophobic probe. A pyrene solution in acetone was prepared first at a concentration of 1 mM. Fixed volumes of this solution were introduced with a micropipet in dust free glass vials, the acetone was allowed to evaporate, and an appropriate volume of the mixed aqueous block copolymer/surfactant solutions was introduced in order to give a final pyrene concentration lower than 3×10^{-7} M. These solutions were allowed to equilibrate overnight and were measured the next day.

Methods. Molecular weights and molecular weight distributions of the precursor block copolymer were determined by size exclusion chromatography (SEC) using a Waters system, composed of a Waters 1515 isocratic pump, a set of three μ-Styragel mixed bed columns, with a porosity range of 10^2 to 10^6 Å, a Waters 2414 refractive index detector (at 40 °C), operated/controlled through Breeze software. Tetrahydrofuran was the mobile phase used at a flow rate of 1.0 mL/min at 30 °C. The setup was calibrated with polystyrene standards having weight-average molecular weights in the range of 2500−900 000 g/mol.

The composition of the precursor diblock and microstructure of the PI block were determined by ^{1}H NMR spectroscopy using a Bruker AC 300 instrument in $CDCl_3$ at 30 °C. By combining the apparent molecular weight values for the PI blocks and the block copolymer, from SEC, with the overall composition of the copolymer precursor, from NMR, and taking into account the known relationships between the PS calibration curves and PI curves, the true molecular weight of the block copolymer precursors could be estimated. The PI−PBMA block copolymer was found to have the following molecular characteristics, $M_{w,copol} = 91\,200$, $M_{w,PI} = 31\,500$, $M_w/M_n = 1.05$, and to contain 34 wt % PI. After hydrolysis and neutralization the NaIMA-1 molecular weight was calculated as $M_{w,copol} = 76\,900$, and its PI content as 41 wt %.

Infrared spectra of the precursors and the final amphiphilic block copolymer were taken in the solid state at room temperature, in the range of 550−5000 cm^{-1}, using a Bruker Equinox 55 Fourier transform instrument, equipped with an attenuated

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total reflectance (ATR) diamond accessory from SENS-IR, by averaging 100 scans at 8 cm^{-1} resolution. IR spectroscopy confirmed the conversion of the *tert*-butylmethacrylate units to methacrylic acid segments (disappearance of the absorption bands at 1394 and 1368 attributed to the *tert*-butyl group).

For dynamic light scattering measurements on aqueous solutions of the block copolymers an AXIOS-150/EX (Triton Hellas) light scattering photometer was employed, equipped with a 30 mW laser source, operating at 658 nm, and an Avalanche photodiode detector. Measurements were made at a fixed scattering angle of 90° and in the temperature range of 25−55 °C on solutions of the amphiphilic block copolymer at different polymer and surfactant concentrations. Heating and cooling cycles were performed allowing sufficient time for sample equilibration between different temperatures. Light scattering intensities were stable within 2% in all experiments. Autocorrelation functions were measured at least six times and analyzed by the cumulants method and the CONTIN routine. One population of diffusing species was resolved in all cases. Polydispersities were evaluated from cumulants analysis, through the second cumulant, and are given as values of the ratio μ_2/Γ^2, where μ_2 is the second cumulant and Γ the decay rate of the correlation function. Apparent hydrodynamic radii, $R_{h,app}$, at different polymer concentrations were calculated by aid of the Stokes−Einstein equation:

$$R_{h,app} = kT/6\pi\eta_o D_{app} \qquad (1)$$

where k is the Boltzmann constant, T the absolute temperature, η_o the solvent viscosity, and D_{app} the diffusion coefficient calculated from the analysis of the correlation function at the particular polymer concentration. The amphiphilic NaIMA-1 sample was found to form micelles in water with a hydrodynamic radius $R_h = 99.5 \pm 1$ nm (after extrapolation to zero concentration) and low polydispersity ($\mu_2/\Gamma^2 < 0.1$). Apparent R_h values were used since the complexes are expected to dissociate at lower concentrations (the I_1/I_3 ratio of pyrene spectra increases by dilution of the solutions of the complexes at constant block polymer/surfactant composition), prohibiting safe extrapolations to zero concentration. Values of R_h have an error of ±2 nm.

The ζ-potential measurements were performed at 25 °C with a ZetaPlus Analyzer (Brookhaven Instruments Corporation) equipped with a 35 mW solid-state laser, operating at $\lambda = 660$ nm. The ζ-potential values determined are the average of 10 repeated measurements (with an error better than ±3 mV).

Steady-state fluorescence spectra of the pyrene probe in aqueous micellar solutions were recorded with a double-grating excitation and a single-grating emission spectrofluorometer (Fluorolog-3, model FL3-21, Jobin Yvon-Spex) at room temperature (ca. 25 °C) using air-equilibrated solutions. The excitation wavelength was $\lambda = 335$ nm, and emission spectra were recorded in the region of 350−500 nm, with an increment of 1 nm, using an integration time of 0.5 s. Slit openings of 1 mm were used for both the excitation and the emitted beam. The I_1/I_3 and I_E/I_M ratios were determined as the average of three measurements (where I_1, I_3 are the intensities of the first and the third peaks of the pyrene fluorescence spectra at 372 and 383 nm, respectively, and I_E, I_M stand for the intensities of excimer fluorescence at 482 nm and monomer fluorescence at 392 nm, respectively) and have an error less than ±0.1 units. The critical micellar concentration (cmc) for the pure NaIMA-1 micelles is found at a concentration of 8.7×10^{-6} g/mL. This value seems to be unchanged in the presence of surfactants, most probably due to the preferred complexation of the

surfactant molecules to the corona chains, leaving a very small number of them free to interact with the micellar core. In such a case alteration of the block copolymer micelles cmc may not be possible.

Results and Discussion

Complexes of DTMAB with NaIMA Micelles. Representative dynamic light scattering results for the system NaIMA/ DTMAB (protocol A) at DTMAB concentrations below its nominal cmc are presented in Figure 1. The light scattering intensity from the solutions increases as the amount of DTMAB increases, indicating an increase in the mass of the aggregates, due to surfactant binding to the anionic sites of the micellar corona. The increase in I_{90} seems to be linear with a break at a DTMAB concentration around 8×10^{-5} g/mL. This break may be an indication of formation of DTMAB micelles on the NaIMA chains above this concentration.[4] Complexation of surfactant molecules on the corona chains will increase the mass of the mixed aggregates in all cases. If formation of micelles incorporating more surfactant molecules (that may be drawn to the vicinity of the polymer chains without direct binding to the corona chains, but just as a result of hydrophobic interactions and micelle formation) is possible, an additional increase in the mass of the complexes may take place, resulting in an abrupt increase in the scattering intensity as in the present case (resembling the case of a cmc). The intensity increase after the break may arise from the increase in the number of micelles.[16] Surfactant binding to polyelectrolytes has been shown to decrease the cmc of surfactants in solution.[1,4,5] Surfactant partition in the block copolymer micellar core is possible and may lead to a decrease in the mass of the copolymer micelles,[4−6] but in the present case the contribution of this mechanism seems to be negligible. On the other hand hydrodynamic radius decreases at first, until a DTMAB concentration of 5×10^{-5} g/mL, and remains constant at higher surfactant concentrations. Most probably, the initial decrease in the radius of the micelles must be a result of the neutralization of charges in the corona chains, coming from the surfactant binding, and a decrease in the interchain electrostatic repulsions. This corona collapse, due to the increase of its hydrophobic character, cannot continue forever, as more surfactant is added, due to space requirements and possibly restrictions to anionic charge accessibility induced by the initially bound surfactant molecules toward the new ones. The fact that the polydispersity of the systems remains low at the whole concentration range investigated seems to preclude the formation of multimicellar aggregates (at least in a large scale) and shows that the observed changes, in mass and size, take place within each block copolymer micelle.

The picture immerging from dynamic light scattering is also supported from ζ-potential measurements (Figure 2). The initial highly negative value of the ζ-potential for the neat block copolymer micelles (−52.5 mV) indicates the presence of stable negatively charged micelles in solution. The ζ-potential decreases in absolute value (but remains negative) as the DTMAB concentration increases. The change in ζ-potential is more abrupt at low surfactant concentrations, while this parameter seems to reach gradually a limiting value as the concentration of the surfactant increases. This behavior can be correlated with the process of the increasing content of surfactant bound to the corona chains, which decreases the overall negative charge of the micelles as more surfactant is present in the system. Furthermore, it may highlight some aspects of the surfactant binding mechanism at the low- and the high-concentration ranges.
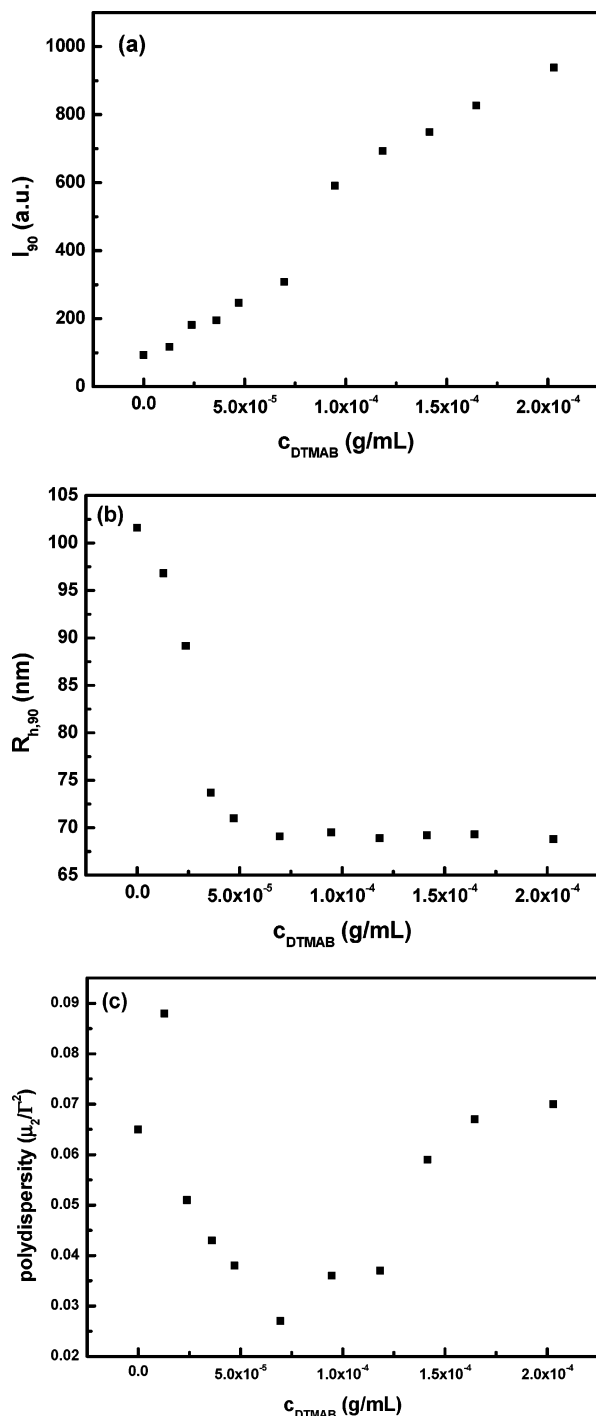
Figure 1. Dependence of (a) light scattering intensity, I_{90}, (b) hydrodynamic radius, R_h, and (c) polydispersity of the NaIMA/DTMAB complexes on DTMAB concentration ($c_{pol} = 2.2 \times 10^{-4}$ g/mL). The lower concentration corresponds to approximately 4% neutralization of total anionic charges in solution, while the higher one corresponds to approximately 60%.

When a solution of DTMAB with a concentration above the cmc is added to the NaIMA micellar solution (protocol B) a similar increase of the light scattering intensity is observed (Figure 3). However, the change in R_h is steeper, and actually no variation of the hydrodynamic radius with surfactant concentration can be seen. R_h remains constant at the concentration range studied at a value which is slightly higher than the one measured for the complexes, at high DTMAB concentration, when the surfactant concentration in the added solution is lower than its cmc (protocol A). This indicates a change in the structure
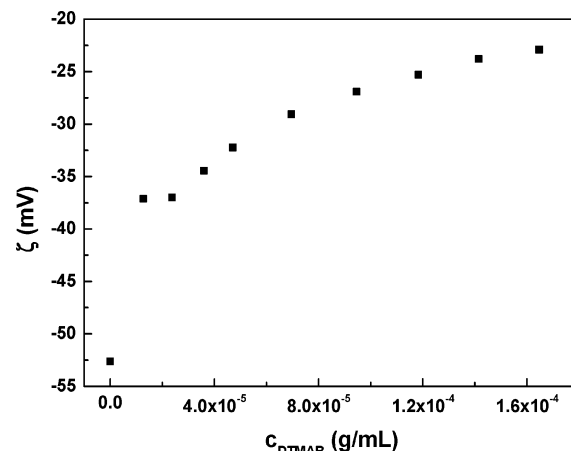

Figure 2. ζ-Potential as a function of DTMAB concentration for NaIMA/DTMAB complexes ($c_{pol} = 2.2 \times 10^{-4}$ g/mL).
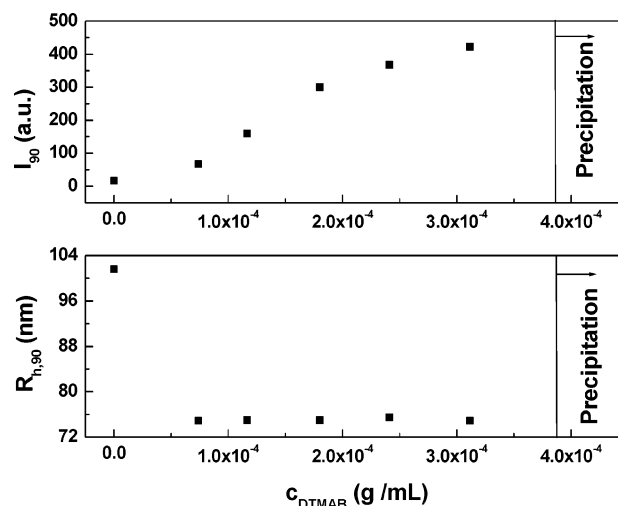

Figure 3. Dependence of light scattering intensity, I_{90}, and hydrodynamic radius, R_h, on DTMAB concentration for NaIMA/DTMAB complexes prepared by addition of DTMAB micellar solutions ($c_{pol} = 2.0 \times 10^{-4}$ g/mL). The vertical line on the right defines the region where precipitation of the complexes takes place.

of the micelles, which may originate from the mode of surfactant binding to the corona in this case. The polydispersity of the system by this preparation protocol is higher (μ_2/Γ^2 values from cumulants analysis range between 0.15 and 0.2) and may indicate some clustering of the micelle/surfactant complexes. This assumption is corroborated by the fact that precipitation is observed at higher final surfactant concentrations (as indicated in Figure 3 by the vertical line).

The ζ-potential measurements (Figure 4) show negative values for this parameter, but now their absolute values increase (become more negative) as the DTMAB concentration increases. It should be noticed that the ζ-potential value at the lowest DTMAB concentration is lower than the corresponding value at the same DTMAB concentration in protocol A. The increase of the negative charge of the particles in solution is unexpected and may indicates that at some point direct complexation of surfactant micelles to the block copolymer micellar corona takes place. Binding of DTMAB molecules would decrease the negative charge of the NaIMA micelles, as is observed at low DTMAB concentrations (Figure 4) and in the solutions of protocol A. The apparent increase of the negative charge in this case may be possible if surfactant micelles are complexed with NaMA chains through some, and not all, of their surface cationic charges. Some internal rearrangement of the complexes involv-
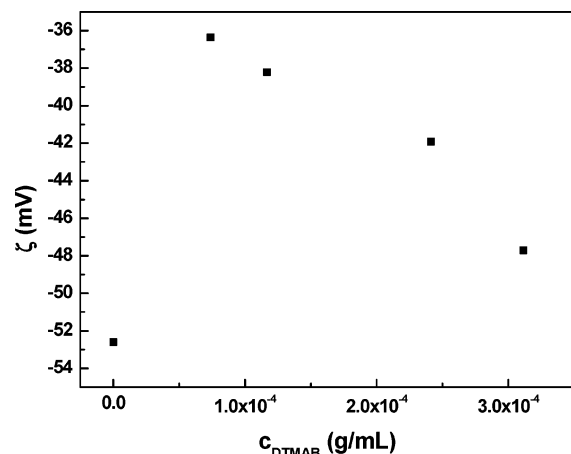
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Figure 4. ζ-Potential as a function of DTMAB concentration for NaIMA/DTMAB complexes, prepared by addition of DTMAB micellar solutions ($c_{pol} = 2.0 \times 10^{-4}$ g/mL).
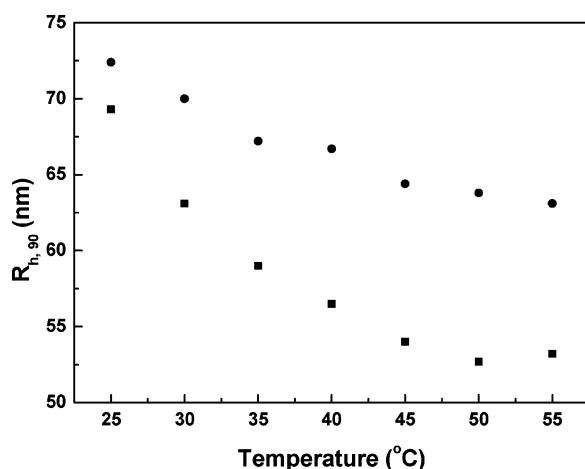

Figure 6. Dependence of hydrodynamic radius, R_h, of the NaIMA/OTMAB complexes on OTMAB concentration ($c_{pol} = 2.1 \times 10^{-4}$ g/mL).

Figure 5. Dependence of R_h on temperature for NaIMA/DTMAB complexes at two different DTMAB concentrations: (●) $c_{DTMAB} = 4.70 \times 10^{-5}$ g/mL and (■) $c_{DTMAB} = 9.46 \times 10^{-5}$ g/mL ($c_{pol} = 2.2 \times 10^{-4}$ g/mL).

ing organization of the initially bound surfactant molecules into hydrophobic domains is also possible as the surfactant concentration increases. This may lead to an actual neutralization degree lower than the calculated one. Alternatively, this apparent increase in the effective negative charge may be related to aggregate formation in the solution of the complexes as dynamic light scattering measurements suggest. The latter scenario seems more realistic.

The complexes formed show a temperature dependence of their dimensions as depicted in Figure 5. The R_h of the particles decreases as the temperature of the solution increases at all surfactant concentrations studied. Within the temperature range studied (25−55 °C) and for DTMAB concentrations above 9 × 10^{-5} g/mL R_h reaches a constant value at the higher temperature range (Figure 5). The temperature dependence of particle dimensions may be attributed to the hydrophobic effect, which increases by an increase in temperature, because of the increase in water mobility.[26] As far as the occurrence of a plateau at higher temperatures and its dependence on DTMAB concentration are concerned, those may be explained as the result of larger hydrophobic domains forming in the NaIMA corona as the DTMAB content increases. Obviously, the corona chains cannot collapse any more, due to spatial restrictions within the spherical brush of the micellar shell, imposed by the corona structure and the formed hydrophobic domains. It should be
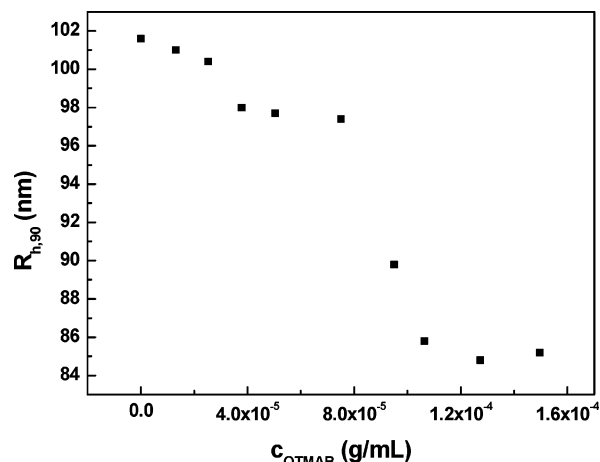
noted that temperature effects on R_h are reversible, i.e., the initial dimensions of the complexes are restored with a decrease in temperature.

Complexes of OTMAB with NaIMA Micelles. To explore possible effects originating from the length of the hydrophobic surfactant tail, complexes between NaIMA micelles and OTMAB have been investigated. The R_h dependence on OTMAB concentration is shown in Figure 6. Here, a steplike decrease in dimensions is observed with an initial slow decrease of R_h, followed by a steeper decrease at $c_{OTMAB} > 7.5 \times 10^{-5}$ g/mL and a plateau at $c_{OTMAB} > 1 \times 10^{-4}$ g/mL. It is of interest that the plateau occurs at higher surfactant concentrations and the R_h plateau value is lower compared to those of the DTMAB case. At the same time I_{90} increases monotonically with c_{OTMAB}, and the polydispersity of the system remains low (at the same range as for DTMAB, i.e., $\mu_2/\Gamma^2 < 0.1$). The first shallow decrease in R_h is difficult to interpret. One explanation may be that a certain surfactant concentration is needed in order to achieve a significant corona collapse. The reason for the R_h plateau in the OTMAB surfactant case at $c > 1 \times 10^{-4}$ g/mL has to be the same as in the case of DTMAB. Corona collapse, due to surfactant complexation, should reach a limit dictated from space requirements within the micellar corona. This argument is supported by the fact that the plateau is observed at a higher concentration than in the DTMAB case. The observed features have to be related to the shorter hydrocarbon chain of OTMAB and the lesser hydrophobic character that induces to the complexes after binding to the micellar corona.

The ζ-potential values as a function of OTMAB concentrations for this system are shown in Figure 7. The ζ-potential shows an abrupt change at the first addition of surfactant and then remains more or less constant up to $c_{OTMAB} \sim 6 \times 10^{-5}$ g/mL. Then its absolute value decreases monotonically, remaining negative in sign. The c_{OTMAB} concentration that the jump in ζ-potential is observed coincides with the jump (decrease) in R_h. Presumably, OTMAB binding to NaMA corona chains in the low-concentration region is low and insufficient to induce sufficient changes to both parameters. Apart from the initial strong decrease of ζ-potential, which may involve OTMAB binding to the outer corona region, one may assume that due to the higher hydrophilicity (shorter hydrophobic tail compared to DTMAB) of the surfactant an increase in its overall concentration is required to facilitate further complexation.

The NaIMA/OTMAB complexes show analogous temperature responsiveness as that described for the NaIMA/DTMAB case.
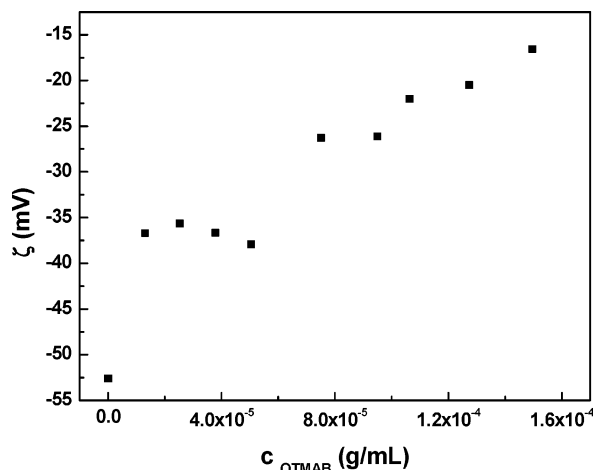
Figure 7. ζ-Potential as a function of OTMAB concentration for NaIMA/OTMAB complexes ($c_{pol} = 2.1 \times 10^{-4}$ g/mL).

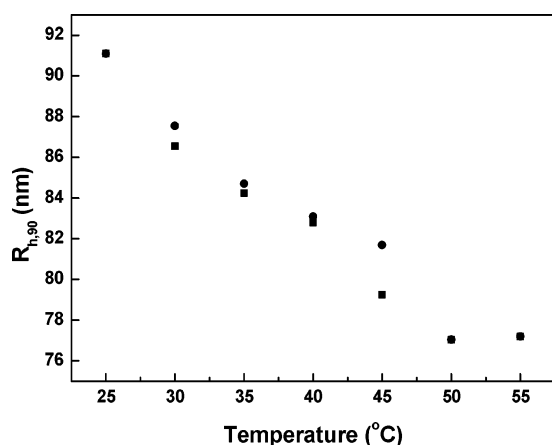**Figure 8.** Dependence of R_h on temperature for NaIMA/OTMAB complexes at $c_{OTMAB} = 1.06 \times 10^{-4}$ g/mL: (■) heating, (●) cooling ($c_{pol} = 2.1 \times 10^{-4}$ g/mL).

Some representative results are shown in Figure 8, where the reversibility of the dimensional changes as a function of temperature, in heating and cooling cycles, is highlighted. It is worth noting that shrinking of the complexes to a certain size, above which no more shrinking is possible, can be observed even at low OTMAB concentrations, and this may be attributed to the shorter hydrocarbon chains that are less deformable in comparison to the DTMAB ones.

To gain additional insight on the nanoscopic structure of the complexes formed in each case, fluorescence spectroscopy was utilized. In these complex systems pyrene is expected to partition in both the block copolymer micellar core as well as into the hydrophobic domains created in the micellar corona after surfactant binding. The measured emission spectra of pyrene show the presence of excimer in all solutions of complexes formed by addition of surfactant solutions with c_{surf} < cmc (protocol A), although the pyrene concentration was kept low (lower than 3×10^{-7} M). I_1/I_3 and I_E/I_M ratios show no significant dependence on surfactant concentration in both systems (Figure 9). I_1/I_3 values are around 1.2 indicating the presence of hydrophobic environments in the system. This is reasonable since both the PI core of the block copolymer micelles, as well as the corona regions where the surfactants are bound, have a hydrophobic character. The I_E/I_M values are found in the range of 0.2−0.6. Since the solutions of NaIMA micelles alone show no excimer formation, it is legitimate to assume that excimer formation is occurring in the hydrophobic
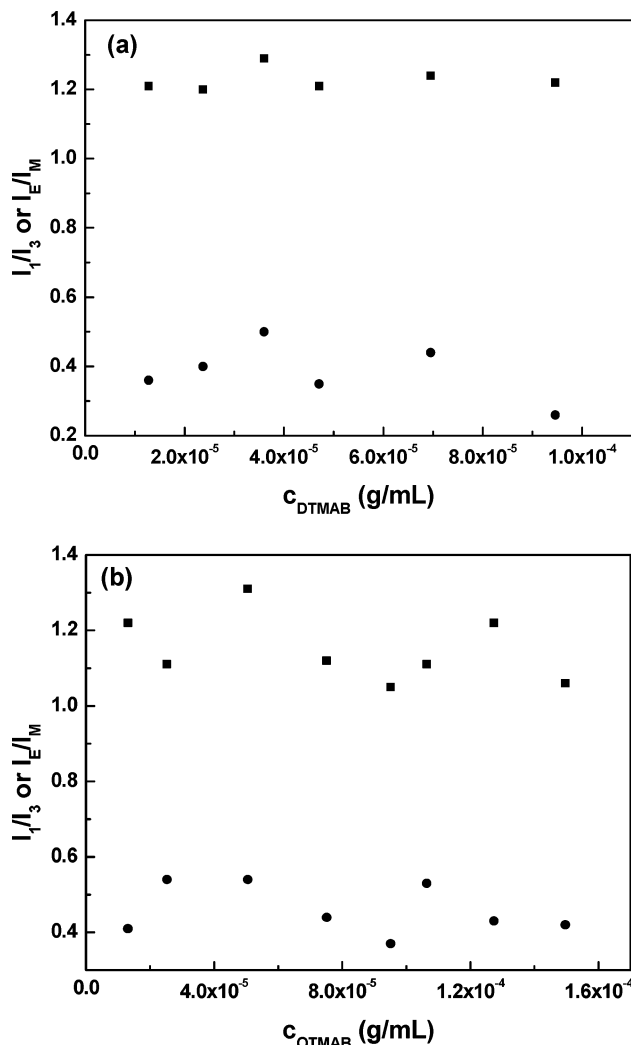

Figure 9. Dependence of the I_1/I_3 (■) and I_E/I_M (●) ratios from pyrene fluorescence emission spectra on DTMAB (a) and OTMAB (b) concentration ($c_{pol} = 1 \times 10^{-4}$ g/mL).

domains formed by the complexed surfactant molecules in the corona region. Excimer formation points to the conclusion that pyrene molecules are highly concentrated in these hydrophobic domains. Additionally, more than one pyrene molecule must be incorporated into single nanodomains. This in turn shows that these domains are very compact and/or their microviscosity is relatively large, in part due to the fact that they are incorporated within already crowded coronal chains, as a result of the micellar core/shell structure.

The situation is somehow different when DTMAB solutions with concentrations higher than the cmc (protocol B) were used for the preparation of the micellar/surfactant complexes. There, excimer formation is observed only at lower surfactant concentrations (c_{DTMAB} < 2×10^{-4} g/mL), with I_E/I_M values lower than 0.18. No excimer was observed at higher concentrations. The latter result suggests that some binding of the original DTMAB micelles takes place on the NaIMA corona, since these surfactant micelles are expected to be more fluid than the hydrophobic domains formed in the block copolymer micelle corona by complexation of single DTMAB molecules.[4,15] Most probably DTMAB micelles must reside in the outer, lower segment density, regions of the corona and may induce some local excess of positive charge. This in turn may lead to some clustering of the micelles/surfactant complexes as light scattering data, i.e., increased scattering intensity and polydispersity, suggest, since cationic surfactant micelles can act as cross-links

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for the negatively charged block copolymer micellar coronas. Clustering of the NaIMA/DTMAB complexes may lead to the formation of species with more negative charge than individual micelles of protocol A, as the ζ-potential measurements in Figure 4 show.

Conclusions

Sodium poly(isoprene-*b*-methacrylate) copolymer, prepared by a combination of anionic polymerization and selective post polymerization functionalization, forms micelles of narrow size distribution in water. Mixing aqueous micellar solutions of NaIMA with solutions of two cationic surfactants, namely, dodecyltrimethylammonium bromide (DTMAB) and octyltrimethylammonium bromide (OTMAB), with different hydrophobic tail lengths, under controllable conditions, led to the formation of water-soluble amphiphilic block copolymer micelles/surfactant complexes. Characterization of the resulting complexes by dynamic light scattering, ζ-potential measurements, and fluorescence spectroscopy, using pyrene as a probe, gave information regarding their structural characteristics as well as the formation process. Properties of the systems were found to depend on surfactant concentration and surfactant type and state in the initial solutions, as well as temperature.

When surfactants are in a nonassociated state in the initial solutions, complexation of individual surfactant molecules at the coronal NaMA chains takes place, followed by an increase in the mass and a decrease in the size of the micelles. These changes are more severe when DTMAB, with the larger hydrophobic tail, is used for complexation. Combined experimental evidence points to the conclusion that individual surfactant micelles complex to the block copolymer micellar corona, when the DTMAB concentration, in the starting solutions, is higher than the surfactant cmc. All complexes show a decrease in their dimensions as temperature increases due to the hydrophobic effect, which is amplified by surfactant complexation.

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