Polymer 51 (2010) 2872–2878

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Small angle neutron scattering study of deuterated sodium dodecylsulfate micellization in dilute poly((2–dimethylamino)ethyl methacrylate) solutions

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ARTICLE INFO

Article history:
Received 4 February 2010
Accepted 10 April 2010
Available online 29 April 2010

Keywords:
Poly((2–dimethylamino)ethyl methacrylate)
Micelle
Small angle neutron scattering

ABSTRACT

Poly((2–dimethylamino)ethyl methacrylate) with 60,000 g/mol and a narrow polydispersity (1.12) was synthesized using group transfer polymerization in order to investigate the structure of poly ((2–dimethylamino)ethyl methacrylate)/sodium dodecylsufate complexes in water. The synthesized polymer chain conformation in water was studied as a function of deuterated sodium dodecylsulfate concentration using small angle neutron scattering. We found three transitions of the poly ((2–dimethylamino)ethyl methacrylate) chain conformation induced by the added deuterated sodium dodecylsulfate. The transitions resulted from interactions between the polymer and the surfactant, so that micelles are formed along the polymer backbone above the critical aggregation concentration. The structure of micelles in a poly((2–dimethylamino)ethyl methacrylate)/deuterated sodium dodecylsulfate solution was analyzed through model fitting of the small angle neutron scattering data measured at the condition where the poly((2–dimethylamino)ethyl methacrylate) was contrast-matched with a mixture of 80% H_2O and 20% D_2O.

1. Introduction

Interactions between polymers and surfactants in water have been investigated because of their potential applications as detergents, [1] rheology modifiers, [2] and gelation agents [3,4]. The surfactants are typically charged, while the polymers are generally neutral or oppositely charged with respect to the surfactants. Depending on whether the polymers are neutral or oppositely charged, mixtures of polymers and surfactants in water show different behavior [5,6]. In cases where anionic surfactants are added to a dilute neutral polymer solution, such as poly(ethylene oxide) (PEO), poly(vinyl pyrrolidone) or poly(vinyl alcohol) in water, the spherical surfactant micelles are wrapped by the polymer chains, which is termed a necklace-like structure, and is formed above the critical aggregation concentration (CAC), which is lower than the critical micelle concentration (CMC) of the surfactant in pure water. This continues with increasing surfactant concentration until the polymers are saturated with micelles [5,7]. Many factors, such as molecular weight, concentration, flexibility and hydrophobicity of the polymer influence the association between the polymer and the surfactant. It has been shown that in dilute or semi-dilute PEO water solutions, necklace-like PEO/sodium dodecylsulfate (SDS) complexes are formed when the PEO molecular weight is high enough [5,7–10]. Spherical micelles wrapped by polymers in semi-dilute solutions should be able to be used to create a templated or structured hydrogel if the polymer is crosslinkable. Poly((2–dimethylamino ethyl) methacrylate) (PDMAEMA) is a water-soluble polymer which can be cationic or neutral depending on pH, [11,12] and can be chemically crosslinked using 1,2–bis(2–iodoethoxy)ethane (BIEE) in water [13,14]. Recently, binding of SDS surfactants to short PDMAEMA (8000 g/mol) chains was observed using small angle neutron scattering (SANS) by Cosgrove et al. at pH 9.1 where the polymer is considered neutral [15]. In the SANS data by Cosgrove et al. a peak was observed in the q range 0.04–0.06 $Å^{-1}$, and q^{-4} power law behavior at low q was observed in dilute PDMAEMA solutions with either deuterated SDS (d-SDS) or hydrogenated SDS in D_2O. They attributed the peak in the scattering to the formation of PDMAEMA/SDS complexes and suggested several short PDMAEMA chains are associated with each micelle, as the chains used in their work had an average degree of polymerization of only about 50, which is lower than expected for the necklace-like structure where several spherical micelles are connected by a single polymer chain [5,8–10,16]. Since a necklace-like structure is one of the

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doi:10.1016/j.polymer.2010.04.018

prerequisites to create a structured PDMAEMA hydrogel templated with SDS micelles, in this work we synthesized 60,000 g/mol PDMAEMA (approximately, ~395 degree of polymerization) using group transfer polymerization (GTP) [17], and the structure of PDMAEMA/SDS complexes in dilute PDMAEMA solutions was investigated using SANS and H/D contrast matching methods.

2. Experimental section

All reagents were purchased from Aldrich, unless otherwise stated. The monomer, ((2−dimethylamino)ethyl methacrylate) (DMAEMA) from Polysciences, Inc., was passed through a basic alumina column to remove the inhibitor and was dried by stirring over calcium hydride for 24 h. The monomer was vacuum-distilled at 45 °C before use. Tetrahydrofuran (THF) from Fisher was refluxed over sodium and benzophenone for 3 days and then distilled. The dried THF was transferred to the reaction flask via a double-tipped needle. The initiator, 1−methoxy−1−trimethylsiloxy−2−methyl−1−propene (MTS), was distilled and stored in a graduated Schlenk flask before use. Tetrabutylammonium bibenzoate catalyst (TBABB) was prepared by the method of Dicker et al. [18] PDMAEMA was synthesized using GTP as described by Armes et al. [11,19] All glassware was heated overnight at 130 °C before use. In order to eliminate surface moisture, assembled glassware was heated under vacuum. 100 ml of dry, distilled THF was transferred into a flask via a double-tipped needle. 5 mg TBABB (2mol% based on initiator) was dissolved in small amount of the dried THF and the solution was transferred into the flask via a double-tipped needle. Then, 0.1 ml MTS was added to the flask. 25 ml of DMAEMA monomer was added dropwise via a double-tipped needle to the solution. The reaction causes the temperature of the solution increase as it is an exothermic reaction. A thermocouple was used to monitor the temperature of the solution during the polymerization. The solution was stirred without additional heating until the solution temperature returned to room temperature. The polymerization was terminated by addition of 10 ml methanol and the solvent was removed using a rotary evaporator at 45 °C. The synthesized polymer was further dried in a vacuum oven for at least 3 days at 45 °C. For the SANS measurements, D_2O and d-SDS were purchased from Cambridge Isotope Laboratories, Inc. To observe the effect of pH on the SANS intensity of the PDMAEMA solutions, PDMAEMA was dissolved in pure D_2O or acidified D_2O. Acidified D_2O was prepared by adding small amount of a 35 wt% DCl solution in D_2O to pure D_2O. Also, a series of 10 mg/ml PDMAEMA solutions in pure D_2O with the desired d-SDS concentrations were prepared by mixing a 20 mg/ml PDMAEMA solution with various concentrated d-SDS solutions in order to investigate the change of PDMAEMA chain conformation resulting from the interactions between PDMAEMA and d-SDS. The size and shape of the micelles in a 10 mg/ml PDMAEMA solution with 100 mM d-SDS was observed under the conditions where the PDMAEMA was contrast-matched to a mixture of 80% H_2O and 20% D_2O. Each solution was measured in a demountable titanium cell with a 1 mm or 2 mm path length for the SANS experiments, depending on the solvent. SANS experiments were carried out at the Center for Neutron Research at the National Institute of Standards and Technology on the 30 m NIST-NG7 instrument [20]. The raw data were corrected for scattering from the empty cell, incoherent scattering, detector dark current, detector sensitivity, sample transmission, and thickness. Following these corrections the data were placed on an absolute scale using direct beam measurement and circularly averaged to produce $I(q)$ versus q plots where $I(q)$ is the scattered intensity and q is the scattering vector ($q = 4\pi\sin\theta/\lambda$). The q range was 0.0046−0.40 $Å^{-1}$ and the neutron wavelength was 6 Å with a wavelength spread $\Delta\lambda/\lambda = 0.11$.

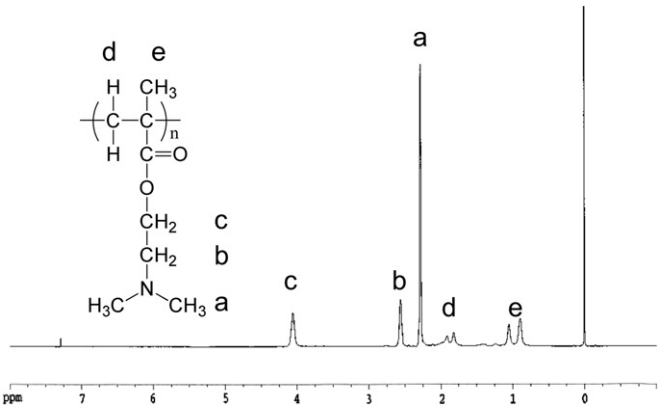

Fig. 1. ^1H NMR of synthesized PDMAEMA in $CDCl_3$.

3. Results

3.1. Polymer characterization

3.1.1. Proton nuclear magnetic resonance spectroscopy (^1H NMR)

The chemical structure of synthesized PDMAEMA, as shown in the insert in Fig. 1, was confirmed using a Bruker 400 MHz ^1H NMR and using $CDCl_3$ with 1% TMS as solvent. The NMR signal at δ 0.8−1.1, assigned to the methyl group in the main chain, indicates the vinyl group of the monomers polymerized.

3.1.2. Gel permeation chromatography (GPC)

GPC was used to determine a PMMA equivalent molecular weight and molecular weight distribution of the synthesized PDMAEMA. A series of near-monodisperse poly(methyl methacrylate) (PMMA) polymers from Polymer Laboratories were used as calibration standards. (Fig. 2) The eluent was HPLC grade THF with 2 vol% triethylamine at a flow rate of 1 ml/min. Here, the molecular weight is reported as PMMA equivalent. Based on the calibration curve, the number-average molecular weight of the synthesized PDMAEMA was 60,000 g/mol with 1.12 PDI which is close to the target molecular weight of 50,000 g/mol. The difference between the measured and the target molecular weight is probably due to the hydrodynamic volume of PDMAEMA being larger than the PMMA used as a calibration standard.

4. SANS results

4.1. Dilute PDMAEMA solutions

The binding of SDS to PDMAEMA has been investigated as a function of SDS concentration in dilute polymer solutions by several authors [15,21]. Three different binding processes were suggested, e.g., (1) at very low concentrations, a non-cooperative PDMAEMA monomer/SDS binding, (2) above the CAC, there is hydrophobically driven cooperative formation of PDMAEMA/SDS micelles, and (3) the onset of formation of free SDS micelles at the saturation concentration. In transition (2), the structure of PDMAEMA/SDS micelles has been studied using SANS [15,21]. In these studies, PDMAEMA in water was regarded as a neutral polymer at pH of 8.6 [21] or 9.1 [15]. PDMAEMA can be charged in water depending on pH. Several authors have investigated the charge behavior of PDMAEMA using proton titration [11,12]. They found that the conjugate acid of the tertiary amine of PDMAEMA has a pK_a ~7. In Fig. 3, squares and circles are the SANS intensity from 10 mg/ml solutions of the PDMAEMA synthesized in this work in pure D_2O at the natural pH 8.5 and acidified D_2O at pH 5.9. At pH

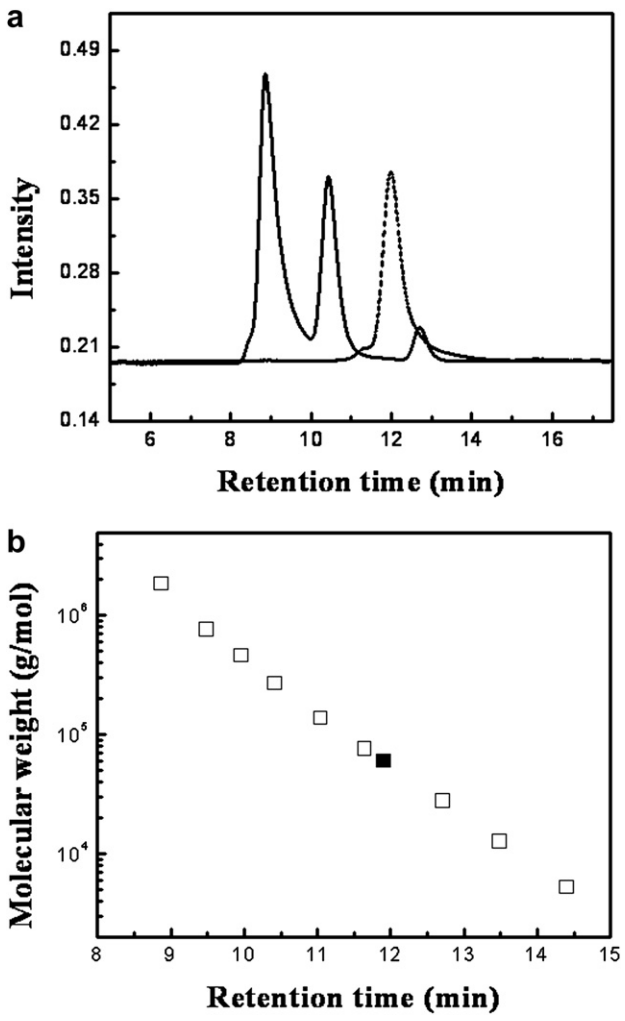

Fig. 2. (a) GPC results of standard PMMAs and synthesized PDMAEMA: PMMAs (solid line) and PDMAEMA (dashed line) and (b) a plot of molecular weight versus retention time: PMMAs (open squares) and PDMAEMA (closed square).

8.5 and pH 5.9, the portion of charged amines per PDMAEMA chain was estimated to be 3% and 92%, from the Henderson–Hasselbalch equation [22] using a pKa of 7. The SANS intensity of both polymer solutions decreases in the q region below 0.03 $Å^{-1}$ resulting in a peak at about $q \sim 0.03$ $Å^{-1}$. The measured SANS intensity in the low q region deviates from a Debye function [23,24] (which describes the form factor of a neutral linear polymer in a dilute polymer solution).

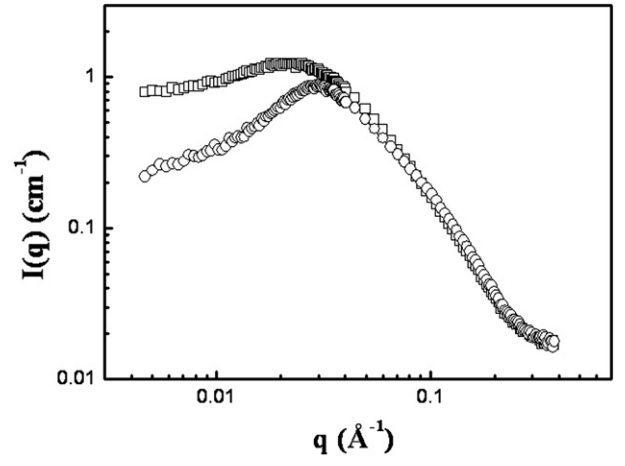

Fig. 3. SANS of 10 mg/ml PDMAEMA solutions in pure D_2O (squares) and acidified D_2O (circles).

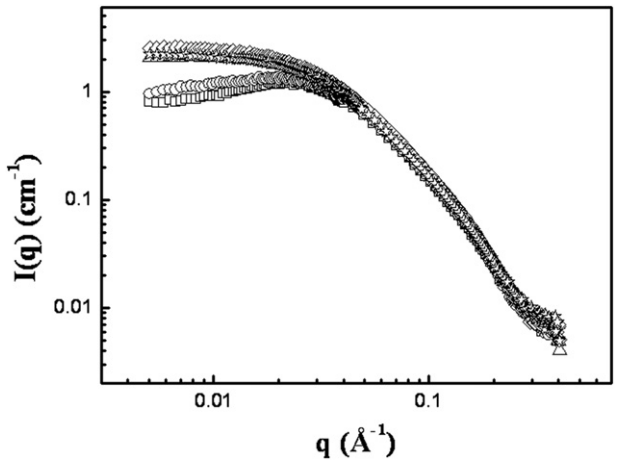

Fig. 4. SANS of 10 mg/ml PDMAEMA solutions with d-SDS in D_2O: 0.0 mM d-SDS (squares), 0.15 mM d-SDS (circles), 0.4 mM d-SDS (triangles), 1.3 mM d-SDS (diamonds), and 3 mM NaCl (no d-SDS) (stars).

The broad peak in the scattered intensity is characteristic of polyelectrolyte solutions and the peak position is generally a function of polymer concentration [25–27]. In general, the scattering peak is thought to result from strong interactions of unscreened charges along the polyelectrolyte chain such that the dynamics are dominated by intra- and inter-chain electrostatic interactions [26]. In contrast to our measured SANS intensity for 10 mg/ml PDMAEMA solutions in pure D_2O at pH 8.5 and acidified D_2O at pH 5.9, the SANS intensity of Cosgrove et al [15]. (for 15,500 ppm PDMAEMA solution in pure D_2O at pH 9.1 and acidified D_2O at pH 2.0) showed monotonically decreasing scattering and were fit using a Debye function. From their fits, it was concluded that the size of the charged polymer in acidic D_2O is nearly twice that measured in pure D_2O due to repulsive electrostatic interactions expanding the charged polymer. Many parameters such as PDMAEMA concentration, the solubility of CO_2 in pure D_2O, the quality of D_2O and so on [22], can affect pH of PDMAEMA solution, resulting variable charge density of the PDMAEMA in pure D_2O. However, the effect is minimized in acidic D_2O. Despite of the lower charge density for PDMAEMA at pH 5.9 compared to PDMAEMA at pH 2.0, our SANS intensity shows a peak characteristic of polyelectrolyte solutions. One possible explanation for this discrepancy might be the fact that our q range is extended to significantly lower q compared to the data of Cosgrove et al. They only published data to $q_{min} \sim 0.02$ $Å^{-1}$ making it difficult to observe the scattering peak.

4.2. Dilute PDMAEMA solutions with d-SDS (0.0 mM ≤ [d-SDS] ≤ 1.3 mM)

Fig. 4 shows the SANS intensity of 10 mg/ml PDMAEMA solutions with d-SDS in D_2O as a function of d-SDS concentration. As d-SDS concentration increases, the SANS intensity in the low q region increases, but does not change in the high q region.

When 1.3 mM d-SDS was added to a 10 mg/ml PDMAEMA solution, the SANS intensity changed to a monotonic decreasing function of angle. The fraction of charged amines per PDMAEMA chain in D_2O at pH 8.5 is about 3%, which corresponds to ~1.9 mM amine groups in the solution being charged. The concentration is

very close to the concentration of added 1.3 mM d-SDS, causing the broad peak in the SANS intensity to disappear. This observation that the change in SANS intensity was induced by the electrolyte nature of d-SDS was confirmed by measuring the SANS intensity of a 10 mg/ml PDMAEMA solution in D_2O containing 3 mM NaCl which also caused the broad peak to disappear, as shown in Fig. 4. Our finding is the same as reported by Amis et al [27]. who measured a similar system based on poly(2–vinylpyridine) (P2VP). In their work, P2VP was partially quaternized with dimethyl sulfate in dimethylformamide. Three separate polymer solutions in deuterated ethylene glycol were measured using SANS: a neutral polymer solution, a polyelectrolyte solution without added electrolyte, and a polyelectrolyte solution with an excess of electrolyte. They found that a broad peak in the SANS for a polyelectrolyte solution without electrolyte disappeared by adding excess electrolyte and the observed scattering profile was nearly identical to the neutral polymer, and concluded that the unusual scattering found in the SANS of polyelectrolyte solutions is electrostatic in nature. Our SANS results indicate that PDMAEMA at our experimental conditions is weakly charged in pure D_2O and that the added d-SDS surfactant acts as an electrolyte, which effectively screens the long-range electrostatic interactions between charged PDMAEMA monomers. Additional evidence of the weak charge density of PDMAEMA in pure D_2O is that all solutions studied within the d-SDS concentration were optically transparent which is in contrast to polycationic/anionic surfactant mixtures which are generally not optically transparent. In general, when anionic surfactants are added to a strongly charged polycationic solution, various thermodynamic states are observed depending on the ratio of the total charge of anionic surfactants to the total charge of the polyelectrolyte. As this ratio increases, the clear solution turns cloudy and precipitates due to charge neutralization are observed. The solution becomes transparent again at an excess level of anionic surfactant [28]. The SANS intensity measured after the charge screening shown in Fig. 4 did not fit a Debye function as D_2O is not a theta solvent for PDMAEMA at 25 °C, which is consistent with the observed power law dependence of I(q) vs q deviating from −2.0 [23,24] (observed −2.13). Among the binding mechanisms of SDS and PDMAEMA in 0.2% w/v solutions with SDS at pH 8.6, it has been suggested by Holzwarth et al., [21] that a non-cooperative process results in PDMAEMA/SDS complexes containing unassociated dodecylsulfate (DS^-) ions attached to the PDMAEMA chain below the CAC (~2.5 mM). It is pointed out that the major changes in the SANS data in Fig. 4 are observed at a similar concentration of d-SDS to Holzwarth's work. Holzwarth et al. attributed the non-cooperative binding to charge–dipole interactions with entropic effects as they ignored the charge density of PDMAEMA. However, we believe the binding of PDMAEMA/d-SDS below 1.3 mM d-SDS can be ascribed to charge–charge interactions. To observe the effect of the binding on the PDMAEMA chain conformation, the radius of gyration (R_g) of a neutral PDMAEMA chain in D_2O, resulting from adding d-SDS or NaCl, was determined from a Guinier plot [23,29]. There was a negligible difference in the R_g of a PDMAEMA chain (~4.5 nm or 4.1 nm) in the presence of d-SDS or NaCl, indicating that the total amount of bound d-SDS is too small to induce a large change of PDMAEMA chain conformation. The Debye function does not fit the data well at high q which leads to an over estimation of the Rg. This is due to the different power law behavior in the high q region ($q^{-2.13}$) for the screened polymer. If the Debye fit is restricted to the low q region ($0.0046 < q < 0.04 Å^{-1}$) then the fit is improved and the R_g obtained from the Debye function is consistent with that obtained from Guinier analysis and the R_gs obtained between PDMAEMA screened by NaCl or d-SDS are equivalent indicating that under these conditions the screening from the relatively high molecular d-SDS charged species does not change the polymer conformation in comparison to an ion such as Cl^-.

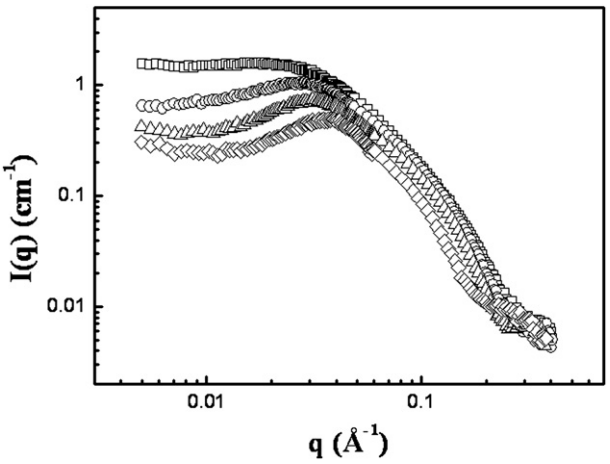

Fig. 5. SANS of 10 mg/ml PDMAEMA solutions with d-SDS in D_2O: 3.0 mM d-SDS (squares), 6.0 mM d-SDS (circles), 12 mM d-SDS (triangles), and 48 mM d-SDS (diamonds).

4.3. Dilute PDMAEMA solutions with d-SDS (3 mM ≤ [d-SDS] ≤ 48 mM)

An important property of ionic surfactants compared to other electrolytes is the hydrophobic effect which causes the surfactants to form micelles above their CMC in water. In general, during the micellization of surfactants in water, the water molecules which are bound to the long hydrophobic tail of a free surfactant molecule are released, leading to increase in the entropy of the system. However, the formation of micelles is opposed due to unfavorable interactions of the charged headgroups which are in close proximity in a micelle. Micellization accompanies the generation of an interface between the hydrophobic core of the micelle and water. In addition, the micellization results in the polar head groups of the surfactants being brought into close proximity of one another at the micelle–water interface. This gives rise to steric repulsions among the head groups. The formation of micelles is controlled by the interplay of these thermodynamic effects. In case of ionic surfactants, the repulsive forces between charged headgroups additionally oppose micellization. As a result, ionic surfactants usually have higher CMCs compared to nonionic surfactants with the same length alkyl chains, often by several orders of magnitude in concentration [30]. It is often observed that when anionic surfactants are added to a neutral polymer solution in water and the polymer interacts with the surfactants, micelles are wrapped by the polymer chains [5,8–10]. Nagarajan proposed two favorable energy terms for the formation of polymer/SDS complexes: a decrease in the hydrophobic interface of the micelle exposed to water, and the removal of the hydrophobic parts of the polymer due to its transfer to the hydrophobic surface of the micellar core [31–33]. In order to investigate the effect of d-SDS at concentrations near the CMC on PDMAEMA chain conformation, the d-SDS concentration was measured above 10 mM. The SANS intensity of 10 mg/ml PDMAEMA solutions in D_2O with d-SDS between 3 mM and 48 mM is shown in Fig. 5. The overall SANS intensity decreased as the d-SDS concentration increased, with the decrease of intensity in the low q range being larger, resulting in a scattering peak, in contrast to the disappearance of the peak in the SANS intensity observed in Fig. 4. The change in the SANS intensity indicates that the added d-SDS induced a large change in the PDMAEMA conformation. Since the neutron scattering length density of d-SDS surfactant

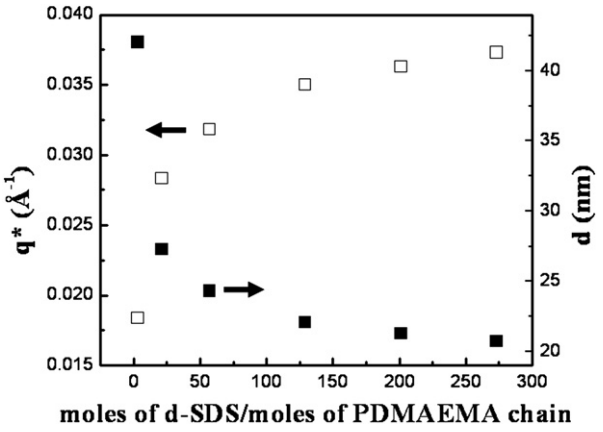

Fig. 6. A change of the SANS peak position (q*) (open squares) and the calculated distance between charged micelles (d) (closed squares) as a function of the ratio of moles of d-SDS to moles of PDMAEMA chain.

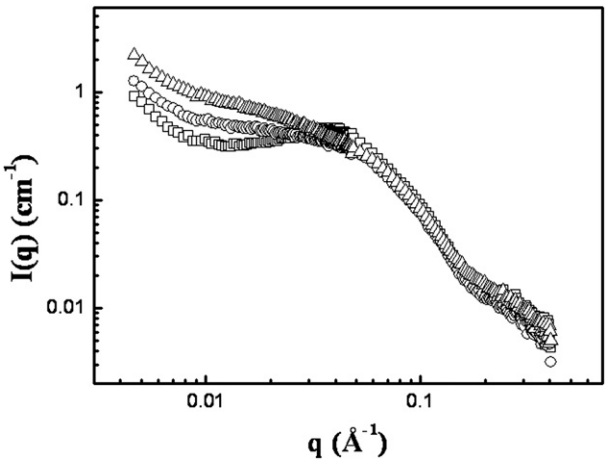

Fig. 7. (a) SANS of 10 mg/ml PDMAEMA solutions with d-SDS in D_2O: 60 mM d-SDS (squares), 100 mM d-SDS (circles), and 150 mM d-SDS (triangles).

(6.736×10^{-6} Å^{-2}) [34] is close to the neutron scattering length density of D_2O (6.34×10^{-6} Å^{-2}), d-SDS micelles should be approximately contrast-matched to the D_2O [9,10,15,35,36].

However, it is unclear whether d-SDS micelles in D_2O polymer solutions remain contrast matched when the micelles incorporate hydrogenated polymer segments in their shell, as this can cause a change in the scattering length density of the resultant mixed micelles. Although we cannot clearly distinguish whether PDMAEMA segments wrapping d-SDS micelles or mixed micelles containing PDMAEMA segments cause the observed peak in the SANS intensity in Fig. 5, we can conclude that PDMAEMA interacts with d-SDS micelles since both scenarios require the participation of PDMAEMA segments in the d-SDS micellization process. Due to the surface charge of the micelle, the micelles interact through long-range electrostatic repulsive interactions which results in a relatively regular distance between micelles. The peak in the SANS intensity reflects this ordering of charged micelles. It is emphasized that the characteristic peak begins to appear in 10 mg/ml PDMAEMA solution at 3 mM d-SDS, which is less than the normal SDS CMC (ca. 8.3 mM [7]). The result indicates that PDMAEMA interacts with d-SDS to make micellization more favorable. Since the peak position shifts to higher q as the added d-SDS concentration increases, more micelles seem to be formed along the PDMAEMA chains. The change of the peak position (q^*) is plotted in Fig. 6 as a function of the ratio (R) of the moles of d-SDS above the CAC (= [d-SDS]−[CAC]) to the moles of PDMAEMA chain. Here, the CAC used were 2.5 mM as measured by Holzwarth et al. [21] With the assumption that d-SDS surfactants are evenly distributed among the PDMAEMA chains, the ratio represents the number of d-SDS surfactants per PDMAEMA chain. The ratio is also helpful to understand how micellization occurs in PDMAEMA/d-SDS solutions, since the ratio provides information about the number of micelles per PDMAEMA chain when the ratio is divided by the aggregation number of d-SDS molecules per micelle. As mentioned before, the origin of the peak is a liquid-like ordering of charged micelles due to electrostatic repulsive interactions between charged micelles.

From the peak position, the average distance of micelles (d) can be estimated, assuming that it has a ordering like amorphous materials in the solutions where the peak position is related to the interdistance by the Bragg relation which was multiplied by a correction factor of 1.23 [37] ($q^* = 1.23 \times 2\pi/d$). It is interesting that when the ratio is 3, the peak was observed at $q^* = 0.018$ Å^{-1} which corresponds to 42 nm. It is not reasonable that only 3 d-SDS molecules can form a micelle, which implies that d-SDS surfactants are not evenly distributed among the PDMAEMA chains. Rather, d-SDS surfactants are localized to some PDMAEMA chains in order to form complete micelles, as micelles are energetically favorable compared to individual d-SDS surfactants. Since d is much larger than the R_g of a neutral PDMAEMA chain in D_2O, the scattering peak represents the interparticle scattering from PDMAEMA/d-SDS complexes. The observed peak position shifts to higher q until the ratio reaches 273, which is well-above the aggregation number of d-SDS surfactants per micelle in water [10] of ~70. At a ratio of 273, each PDMAEMA chain contains ~3.9 d-SDS micelles if we assume that the aggregation number of d-SDS per micelle in the PDMAEMA solution is comparable to that in water. In Fig. 6, q^* increases as the number of charged micelles increases, and q^* is proportional to $R^{0.1}$ where R is the number of d-SDS molecules per PDMAEMA chain. The behavior is similar to a spherical charged particle solutions [25,38,39] where q^* follows the scaling law, $q^* \sim N_P$, with $n = 1/3$, where N_P is the number of particles in solution. The difference in the exponents is probably due to several reasons. First, for our case, R represents the number of d-SDS surfactants per PDMAEMA chain, not the number of particles per PDMAEMA chain. Second, this scaling law should not be over-interpreted as the scattering from the free PDMAEMA chain segments connecting the micelles overlaps in the q region for the ordering of the micelles. It is noted that the spacing between charged micelles in the solution is much larger than the R_g of the neutral PDMAEMA chain in D_2O. This indicates that as charged micelles are formed along a PDMAEMA chain, the occupied volume of the polymer chain increases to minimize electrostatic repulsive interactions between the micelles.

4.4. Dilute PDMAEMA solutions with d-SDS (60 mM ≤ [d-SDS] ≤ 150 mM)

In PEO/water solutions with ionic surfactants, when micelles are connected by a single PEO chain, an increase in viscosity is observed with increasing surfactant concentration until the polymer chains are saturated with micelles. This is explained by stretching of the PEO chains due to the electrostatic repulsion between the SDS micelles [40,41]. Power law behavior in the low q region has been observed by SANS for the PEO/SDS system [9,10] and for star-shaped poly(ethylene glycol)/SDS solutions [35] due to the stretching of the polymer chains. We observed similar behavior in SANS when the d-SDS concentration was above 60 mM. Fig. 7 shows the SANS intensity of 10 mg/ml PDMAEMA solutions in D_2O at d-SDS concentrations between 60 mM and 150 mM. At 60 mM d-SDS, an

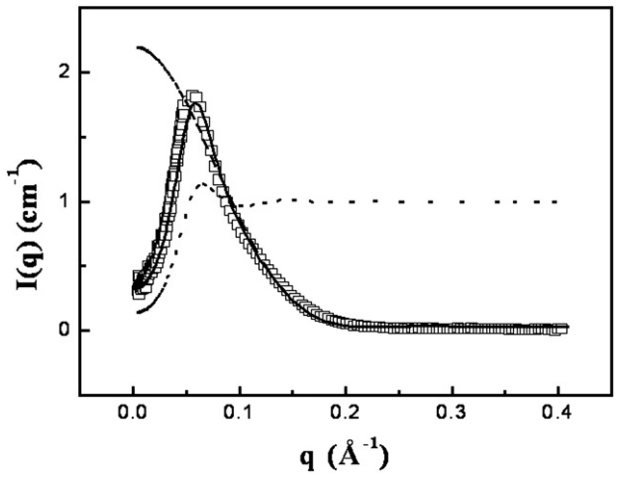

Fig. 8. SANS intensity of 10 mg/ml PDMAEMA solution with 100 mM d-SDS where PDMAEMA was contrast-matched to a mixture of 80% H_2O and 20% D_2O. (squares) The solid line represents the fit to a core-shell model with the rescaled MSA closure. The form factor and the structure factor are shown as a dashed line and a dotted line, respectively.

upturn appeared in the low q region and the correlation peak is observed as in Fig. 5. Above 100 mM d-SDS, the low q upturn in intensity becomes more pronounced and the correlation peak shape is partially hidden. It is notable that the SANS intensity shows a power law behavior in both the low q and high q regions. In the high q region, the observed power law behavior of $q^{-1.3}$ is consistent with a stretched polymer chain in solvent [23,29]. The exponent should be −5/3 for a fully swollen chain and −2 for a Gaussian chain. When monomers are strongly repulsive, as in polyelectrolytes, the exponent is expected to be −1. Since forming micelles along a PDMAEMA chain is more favorable than free d-SDS micelles, the number of the charged micelles per PDMAEMA chain increases as the d-SDS concentration increases, resulting in significant chain stretching and the high q power law tending toward −1.

4.5. A model fit of 100 mM d-SDS in a 10 mg/ml PDMAEMA solution

In order to investigate the structure of the micelles, a mixture of 80% H_2O and 20% D_2O (neutron scattering length density: $\rho = 0.82 \times 10^{-6}$ Å^{-2}) was used as solvent to contrast match the PDMAEMA chains ($\rho = 0.8 \times 10^{-6}$ Å^{-2}) [42]. The measured SANS intensity of 100 mM d-SDS in 10 mg/ml PDMAEMA solution is shown as squares in Fig. 8. Since the correlation peak between the micelles is still observed when PDMAEMA is contrast matched, this supports that the peak shape in Fig. 7 was smeared due to the scattering from the PDMAEMA chains interconnecting the micelles. The size and shape of the micelles in solution was obtained by fitting the data with the Hayter–Penfold model for the scattering. Generally, the size of ionic micelles in water is determined by a balance between the area of the micelle–water interface per surfactant molecule and the charged headgoup repulsion per surfactant molecule [43]. The former decreases as the aggregation number of surfactant per micelle increases and favors growth of the micelle. However, the latter increases with an increase in the aggregation number, opposing a growth of the micelle. When electrolytes or polyelectrolytes are added to spherical ionic micelle solutions, the added electrolyte molecules screen the electrostatic repulsions between charged headgroups, leading to the transformation of spherical micelles into ellipsoidal or worm-like micelles [28,44,45]. Since PDMAEMA is very weakly charged in water, the SANS intensity was fit to a spherical core-shell model with the rescaled mean spherical approximation (MSA) closure [46–48]. The fit result is shown as a solid line in Fig. 8. The form factor and the structure factor were separated using the model, and are shown as a dashed line and a dotted line, respectively. In the fitting process, the core radius of the micelle was constrained to be less than 16.7 Å, which is the length of a fully extended dodecyl chain of SDS [49], and the neutron scattering length densities of the core and solvent were fixed at 6.97×10^{-6} Å^{-2} and 8.2×10^{-7} Å^{-2}, respectively. The neutron scattering length density of the core was calculated, assuming that the core is composed of methyl, and methylene groups in d-SDS [34,49]. However, the scattering length density of the shell was left as a floating parameter to allow the participation of PDMAEMA segments in the micelle shell. In calculating a structure factor, 2.5 mM CAC [21] was used to calculate the electrolyte concentration in the solution. The core radius and the shell thickness of a spherical SDS micelle wrapped by PDMAEMA obtained from the fit were 16.7 ± 0.1 Å and 6.0 ± 0.1 Å, respectively. The scattering length density of the shell was $3.72 \times 10^{-6} \pm 0.1 \times 10^{-6}$ Å^{-2}, implying that PDMAEMA segments are incorporated into the shell. The surface charge per micelle was 15.8 ± 0.1, less than the value of 23.5 for free SDS micelles in water [49].

5. Conclusions

PDMAEMA with 60,000 g/mol and a narrow polydispersity, 1.12, was synthesized using GTP. The conformation of the synthesized polymer in PDMAEMA/d-SDS solutions was investigated as a function of d-SDS concentration using SANS. It was observed that when PDMAEMA was dissolved in D_2O or in acidified D_2O, the polymer shows polyelectrolyte behavior as the tertiary amines in the chain are charged. The polyelectrolyte behavior can be screened by adding 1.3 mM d-SDS or 3 mM NaCl in the solution, which balances 1.9 mM charged amine groups in a 10 mg/ml PDMAEMA solution. The result indicates that the added d-SDS acts as electrolyte, screening the charges and a neutral PDMAEMA chain conformation is restored. Above 3 mM d-SDS, SANS intensity shows a correlation peak from the charged micelles formed along the PDMAEMA chains. d-SDS micellization in the PDMAEMA solution starts below the normal SDS CMC, which indicates that the PDMAEMA chains provide favorable interactions which enhance d-SDS micellization. As the d-SDS concentration is increased, the observed scattering peak position shifts to higher q, indicating more charged micelles are associating per PDMAEMA chain. In spite of the increasing unfavorable repulsive interactions between micelles, the charged micelles associate with the PDMAEMA chains in preference to free d-SDS micelles as the unfavorable interactions are relieved by stretching of the PDMAEMA chain, as evidenced by the power law behavior in SANS scattering. The structure of charged micelles in a PDMAEMA/d-SDS solution was investigated by SANS at the condition where the PDMAEMA was contrast-matched with a mixture of 80% H_2O and 20% D_2O. It was found through a model fit that spherical micelles are formed in the solution and the neutron scattering length density of the shell calculated from the fit shows that the PDMAEMA segments are incorporated into the micelle shell to provide shielding to reduce the hydrophobic interface of the micelle exposed to water.

Acknowledgements

This work utilized facilities supported in part by the National Science Foundation under Agreement No. DMR-0454672. We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the neutron research facilities used in this work.

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