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The Remarkable “Flip−Flop” Self-Assembly of a Diblock Copolymer in Aqueous Solution

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ABSTRACT: In this paper, it is shown that tertiary amine methacrylate-based diblock copolymers can form both micelles and reverse micelles in aqueous solution at room temperature. This remarkable behavior is due to subtle variations in the hydrophilic−hydrophobic balance of the two block sequences, which are based on 2-(diethylamino)ethyl methacrylate (DEA) and 2-(*N*-morpholino)ethyl methacrylate (MEMA). ^{1}H NMR spectroscopy studies indicate that these DEA−MEMA copolymers dissolve molecularly in water at pH 6−7 at 20 °C. DEA−core micelles are formed at higher pH, and MEMA−core micelles are formed at pH 6.5 in the presence of 1.0 M Na_2SO_4. Both types of micelles were characterized in terms of their intensity-average diameters and mean aggregation numbers using dynamic and static light scattering, respectively. In addition, one of the copolymers (60 mol % MEMA, $M_w = 30\,000$, $M_w/M_n = 1.05$) was selected for a detailed small-angle neutron scattering (SANS) study. SANS data for the micelles were analyzed in terms of a weakly interacting polydisperse sphere model and were in reasonable agreement with the light scattering data. The DEA−core micelles are larger than the MEMA−core micelles, but both light scattering and SANS data indicated that the DEA−core micelles had a lower mean aggregation number than the MEMA−core micelles. This suggests that the MEMA−core micelles are relatively dense and compact compared to the more loosely packed DEA−core micelles.

Introduction

It is well-known that AB diblock copolymers undergo micellar self-assembly in solvents which are selective for either block.[1−7] It is also possible to obtain both micelles and so-called reverse (inverted) micelles from the same diblock copolymer by choosing appropriate selective solvents. For example, styrene−butadiene diblock copolymers can form micelles[8] with either polystyrene cores (in *n*-alkanes) or polybutadiene cores (in DMF or MEK). Similarly, it is well-known that small molecule surfactants can form micelles and reverse micelles in aqueous and nonaqueous media, respectively.

Recently, we used group transfer polymerization (GTP) to synthesize a new class of hydrophilic−hydrophilic diblock copolymers based on three tertiary amine methacrylate monomers: 2-(dimethylamino)ethyl methacrylate [DMA], 2-(diethylamino)ethyl methacrylate [DEA], and 2-(*N*-morpholino)ethyl methacrylate [MEMA]. The water solubility of each corresponding homopolymer depended subtly on the solution pH, temperature, and salt concentration. During our studies of the aqueous solution properties of the diblock copolymers, we realized that certain DEA−MEMA diblocks were capable of forming both micelles with either the A block in the core or the B block in the core, *solely in aqueous media at room temperature* (see Figure 1). As far as we are aware,[9] this remarkable behavior remains unique: no other block copolymer, or, indeed, small-molecule surfactant, can exist as unimers, micelles, and reverse micelles in aqueous solution.

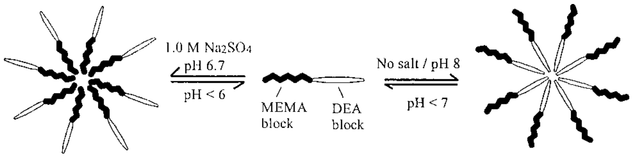

Figure 1. Schematic representation of the formation of micelles and reverse micelles for a DEA−MEMA diblock copolymer at 20 °C.

An account of our preliminary results with one of these DEA−MEMA diblock copolymers has already appeared.[10] Herein, we present our studies for several DEA−MEMA block compositions and include both static light scattering (SLS) and small-angle neutron scattering data for the micelle structures.

Experimental Section

Block Copolymer Synthesis. Tertiary amine methacrylates contain no labile protons and can be polymerized directly via GTP without protecting group chemistry. Accordingly, three DEA−MEMA diblock copolymers were synthesized, with DEA contents varying from 27 to 50 mol % (see Table 1). Both MEMA (Polysciences Inc.) and DEA (Aldrich) monomers were each passed through basic alumina columns, stirred over calcium hydride, and then stored at below 0 °C. Each monomer was distilled under reduced pressure before being transferred into the reaction vessel by cannula. Each copolymer was prepared using a 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS) initiator and *n*-tetrabutylammonium bibenzoate (TBABB) catalyst at 25 °C in dry THF (see Figure 2). In each case, the DEA monomer was polymerized first. The crude diblocks contained 5−10% of DEA homopolymer, which could

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Table 1. Copolymer Compositions, Number-Average Molecular Weights, and Polydispersities for DEA and MEMA Homopolymers and the Three DEA−MEMA Diblock Copolymers

sample code	(co)polymer type	theoretical DEA content (mol %)	exptl. DEA content[a] (mol %)	M_n (theory) (g mol^{-1})	M_n (exptl.) (g mol^{-1})[b]	M_w/M_n[b]
VB51	DEA	100	100	5 850	5 650	1.11
VB27	MEMA			5 350	4 950	1.10
VB63	DEA−MEMA	28	27	7 000	10 100	1.12
VB256A	DEA−MEMA	45	40	19 100	24 700	1.10
VB257	DEA−MEMA	55	50	17 000	25 900	1.06

[a] As determined by ^{1}H NMR spectroscopy. [b] As determined by GPC.

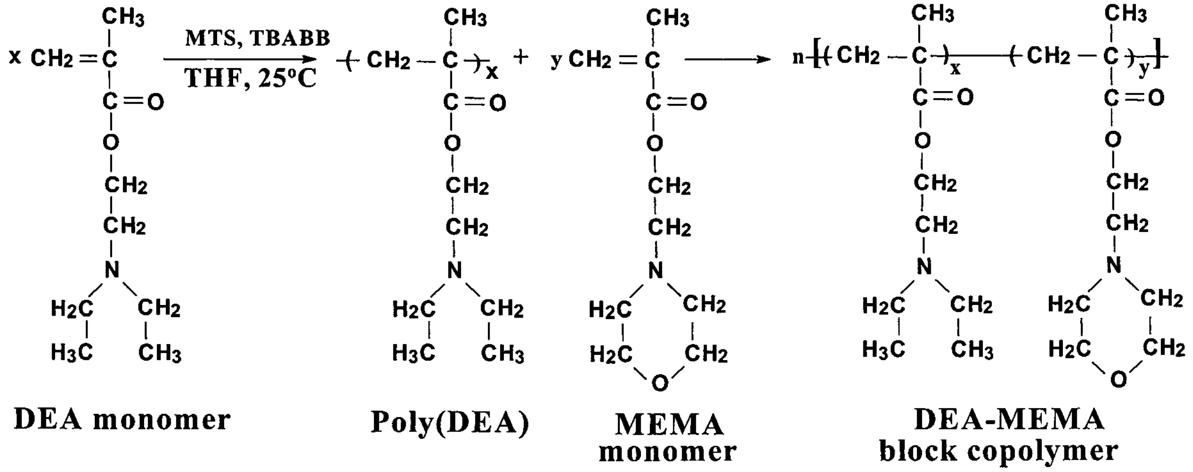

Figure 2. Synthesis of a DEA-MEMA diblock copolymer using group transfer polymerization (GTP) and sequential monomer addition (DEA polymerized first).

easily be removed by selective precipitation into *n*-hexane (a solvent for DEA homopolymer but not for the diblock copolymers). GPC analysis of the purified diblock copolymers indicated low polydispersities (M_w/M_n's were 1.12, 1.05, and 1.06 for the 27, 40, and 50 mol % DEA copolymers, respectively).

Copolymer Characterization. Gel Permeation Chromatography. Molecular weights and molecular weight distributions of all three copolymers were determined using gel permeation chromatography (GPC). The GPC setup consisted of a Perkin-Elmer LC pump and a refractive index detector; the GPC columns were either mixed "E" or mixed "D" (Polymer Labs), and PMMA standards (ex. Polymer Labs), ranging from 680 to 53 000 g mol^{-1} were used for calibration. The GPC eluent was HPLC-grade THF stabilized with BHT, at a flow rate of 1 mL min^{-1}.

Nuclear Magnetic Resonance Spectroscopy (NMR). The compositions of the three block copolymers and their micellization behavior in D_2O were investigated using either Bruker AC−P 250 or 300 MHz instruments and $CDCl_3$ or D_2O/NaOD or D_2O/DCl solvents. Block copolymer compositions were determined by ^{1}H NMR spectroscopy and were in good agreement with the expected values. The compositions were determined by comparing peak integrals of the four $-CH_2OCH_2-$ protons in the MEMA residues at δ 3.7 with those from ester $-OCH_2-$ protons of both MEMA and DEA residues at δ 4.1 in $CDCl_3$. In addition, the same molar ratios were also obtained in D_2O by comparing peak integrals of the four MEMA $-CH_2$-OCH_2- protons at δ 3.7 with the six DEA amine methyl protons at δ 1.3.

Hydrogen Ion Titration. The DEA and MEMA homopolymers and the 40:60 DEA−MEMA diblock copolymer were first dissolved in dilute HCl (pH 2). These solutions contained 1.5 $\times$ 10^{-2} mol dm^{-3} tertiary amine residues. During the titration of the (co)polymer solution by the dropwise addition of 0.5−1.0 M NaOH solution, the solution pH was monitored with a Corning Check-Mite pH meter (precalibrated with pH 4, 7, and 10 buffers).

Dynamic Light Scattering Studies (DLS). The hydrodynamic diameters of diblock copolymers in aqueous solution were measured using a Malvern 4700 dynamic light scattering instrument equipped with a 80 mW argon ion laser operating at λ_o = 488 nm and a series 7032 Multi-8 correlator. The measurements were performed at a fixed angle of 90°, and data were fitted using both monomodal cumulants analysis and the CONTIN algorithm. All measurements were carried out using 1 w/v% copolymer solutions, and the temperature was controlled to $\pm$ 0.1 °C.

Static Light Scattering Studies. SLS measurements on the 40:60 DEA−MEMA block copolymer were carried out using a Sofica instrument, equipped with a He−Ne laser (vertically polarized; λ = 633 nm) and a digital voltmeter, in the angular range from 30 to 150 °C. Refractive index increments, d*n*/d*c*, of both unimers (in THF) and micelles in aqueous solution were determined using a Brice-Phoenix differential refractometer (λ = 633 nm). Before determining the d*n*/d*c* for a MEMA−core micellar solution in the presence of 1.0 M Na_2SO_4 and at pH 6.5, the solution was dialyzed against 1.0 M Na_2SO_4 solution at the same pH. SLS studies were carried out over the concentration range 0.12% to 0.60%.

Small Angle Neutron Scattering (SANS). The LOQ time-of-flight instrument on ISIS at the Rutherford Appleton Laboratory, U.K., was used.[11] The absolute scattering probability $I(Q)$ (cm^{-1}) was measured as a function of momentum transfer Q (Å^{-1}) = $(4\pi/\lambda)\sin(\theta/2)$ with λ the incident neutron wavelength (2.2 → 10 Å) and θ the scattering angle (<10°). This configuration resulted in an accessible Q-range of 0.008−0.20 Å^{-1}. D_2O was used to achieve good contrast between the micelles and the solvent, and copolymer solutions were contained in 2 mm path-length Hellma cells, thermostated to within $\pm$ 0.1 °C of the desired temperature (20, 16, or 8 °C). The intensity scale was calibrated with reference to an accepted standard.[12] Experimental details, data processing, and analysis procedures are described elsewhere.[11] As might be expected from their chemical structures, there was very little contrast between the DEA and MEMA blocks. The micellar solutions were strong scatters, but we were unable to distinguish between the micelle cores and the micelle coronas. Such contrast would require selective deuteration of one of the blocks.

For dilute, aggregated systems, initial estimates for the micelle radius R were obtained using the Guinier law, which is valid at low Q.

$$\ln[I(Q)] = \ln[I(0)] - \frac{(QR_g)^2}{3} \qquad R = \sqrt{5R_g/3} \tag{1}$$

In the above equation, $I(0)$ is an intensity factor related to concentration and contrast. An alternative method to obtain R is from high Q behavior using a Porod plot, $I(Q)Q^4$ versus Q, from which the first peak maximum Q_{max} is related to the radius via $R = 2.7/Q_{max}$ for monodisperse spheres, and $2.2/Q_{max}$ for the polydisperse model described below (with $p \sim 0.20$).

More detailed analyses were carried out using the FISH model least-squares-fitting suite[11] which allows various structural models to be tested, for example, Gaussian coils spheres, cylinders, disks, and ellipsoids (both monodisperse and polydisperse), as well as the incorporation of different structure factors. Instrument resolution was also included. For micelles of volume V and radius R at a number density N, the intensity $I(Q)$ may be written

$$I(Q) = \{N\Delta\rho^2 V^2\} P(Q, R) S(Q, R) \tag{2}$$

Where $\Delta\rho = (\rho_{mic} - \rho_w)$ represent coherent scattering length densities ρ_{mic} and ρ_w for hydrocarbon micelles and D_2O, respectively. $P(Q, R)$ is the particle form factor, which depends on micellar size and shape, whereas $S(Q, R)$ is the structure factor accounting for interactions. In the modeling, it was also necessary to incorporate polydispersity, and a Schultz distribution defined by an average radius R^{av} and RMS deviation $\sigma = R^{av}/(Z + 1)^{1/2}$ where Z is the width of the distribution.[13] The "polydispersity index" p quoted here is σ/R_c^{av}. A hard-sphere model was used for $S(Q)$, and although this is an approximation, it accounts for the general features of interparticle scattering. In any case, $S(Q)$ was only significant for the most concentrated samples at a micelle volume fraction, ϕ, of around 0.10. For the majority of cases ϕ was less than 0.05 (see Table 4), and then it was only necessary to use a form factor. For nonaggregated (unimer) systems, at concentration c (in grams per cubic centimeters), the scattering may be interpreted in terms of a random Gaussian coil with radius of gyration R_g, via eq 3.[14]

$$I(Q) = \left\{\frac{(b_1 - b_2\bar{V}_1/\bar{V}_2)^2 c N_A N_1{}^2}{M_w}\right\} \left[\frac{2(\exp(-(QR_g))^2 + (QR_g)^2 - 1)}{(QR_g)^4}\right] \tag{3}$$

The terms b_1 and $\bar{V}_i$ represent the sum of coherent scattering lengths and the molar volume for component i with 1 and 2 denoting the polymer and solvent, respectively. N_1 is the number of segments per chain, and N_A is the Avagadro number. Hence, $(b_1 - b_2\bar{V}_1/\bar{V}_2)$ is the contrast factor which may be calculated knowing the isotopic composition and assuming a mass density of 1.00 g cm^{-3} for the copolymer. Equation 3 assumes ϑ (or near ϑ) conditions and monodisperse chains. In eqs 2 and 3, the collected terms in curly brackets represent absolute intensity scale factors (*sf*) which may be used as a cross-check on the model. Agreement between fitted absolute scale factors and those based on known quantities was always better than 10%, suggesting that the models employed are physically realistic.

Surface Light Scattering. For "high value" surfactants such as these diblock copolymers, where sample volume is a consideration, surface light scattering has an important advantage over traditional surface tension techniques such as the du-Nouy ring, since only small solution volumes are required. The thermally roughened surface of a liquid can be considered to be a Fourier wave series, each having a well-defined wavelength Λ and frequency ω. The temporal behavior of the waves depends on both bulk and surface properties such as density, viscosity, surface tension, and elasticity.[15] Each capillary wave decays with time so that $\omega = \omega_0 + i\Gamma$, with Γ the damping constant. The wavenumber may be defined as $q = 2\pi/\Lambda$. For a monolayer-covered liquid surface, ω and q are related by a dispersion equation which includes a transverse (γ) and dilational (ϵ) modulus, accounting for the surface tension γ_0 and the Gibbs elasticity ϵ_0. With these particular diblock copolymers, it was only possible to obtain reliable values for γ_0; hence, elasticities are not quoted. Details of the surface light scattering setup, experimental procedure, and data analysis are given elsewhere.[15,16] By use of this equipment, a q-range between 235 and 613 cm^{-1} could be studied. To aid temperature control (22 ± 0.1 °C) and to prevent airborne vibrations, samples were contained in clean watchglasses and then placed inside a thermostated airtight box. An equilibration time of about 1 h was allowed before data were recorded. Noise levels of the averaged correlation functions were generally about 0.5%.

Results and Discussion

GTP was used to synthesize both DEA and MEMA homopolymers and a series of three DEA−MEMA block copolymers (see Figure 2) with DEA contents ranging from 27 to 50 mol %. GTP and NMR results are summarized in Table 1. Polymerizations were carried out by first polymerizing the DEA monomer, followed by the second monomer (MEMA). The number-average molecular weights (M_n) and the polydispersities (M_w/M_n) of the (co)polymers were determined by GPC and are summarized in Table 1. In general, good agreement was observed between the target and observed values of M_n. All (co)polymers had low polydispersities (<1.12), which are characteristic of GTP syntheses.[17] The M_n of the DEA homopolymer was also calculated from its NMR spectrum, by comparing the integral of the $-OCH_3$ protons of the MMA endgroup (derived from the MTS initiator) at δ 3.6, with the integrals of any of the other DEA signals.[11]

Aqueous Solution Properties of DEA and MEMA Homopolymers. MEMA homopolymer is a weak polybase which is water-soluble in both neutral and acidic media at 20 °C. However, it precipitates from neutral or basic aqueous solutions at 34−54 °C, depending on molecular weight.[18] When such solutions are cooled, the polymer becomes soluble again. This thermoreversibility has also been observed by many researchers with different neutral polymers based on methyl vinyl ether (MVE), methyl triethylene glycol vinyl ether (MTEGVE), *N*-isopropylacrylamide, ethylene oxide, and so on. For example, in the MTEGVE−MVE system,[19] the differences between cloud-points of the related blocks are around 30 to 40 °C. As the solution temperature increases, one block becomes partially dehydrated and forms a micelle core while the other block is still solvated.

It was also observed that MEMA homopolymer can be precipitated (salted out) relatively easily from aqueous solution on addition of electrolytes such as Na_2SO_4. However, a MEMA homopolymer can be redissolved as a cationic polyelectrolyte by the addition of acid even at high salt concentration due to protonation of the morpholine groups. In contrast, the DEA homopolymer was completely insoluble in aqueous media at both neutral and basic pH at room temperature. This is due to the increasing hydrophobicity of the substituents on the tertiary amino nitrogen atom. However, the latter homopolymer dissolved readily in acidic aqueous solution (pH 3−4) due to protonation of its tertiary amine groups. In addition, the DEA homopolymer became more soluble as the solution temperature was lowered to 5 °C.

Table 2. Summary of the Hydrodynamic Diameters, Polydispersities, and Mean Aggregation Numbers of 1.0 % DEA−MEMA Diblock Copolymer Solutions at 20 °C

					micelle diameter/nm[c]	
sample code	DEA content[a] (mol %)	M_n (exp.) (g mol^{-1})[b]	pH	Na_2SO_4 conc (mol dm^{-3})	DEA core d/(PD)	MEMA core d/(PD)
VB63	27	10 100	<7	no salt	unimers	unimers
VB63	27	10 100	8	no salt	21 (0.230)	
VB63	27	10 100	6.5	1.0		aggregates
VB256A	40	24 700	<7	no salt	unimers	
VB256A	40	24 700	8.5	no salt	33 (0.057)	
VB256A	40	24 700	6.5	1.0		26 (0.022)
VB257	50	25 900	<7	no salt	unimers	
VB257	50	25 900	7.5	no salt	35 (0.122)	
VB257	50	25 900	6.5	1.0		29 (0.031)

[a] As determined by ^1H NMR spectroscopy. [b] As determined by GPC (vs PMMA calibration standards). [c] As determined by dynamic light scattering at 90° (PD = polydispersity).

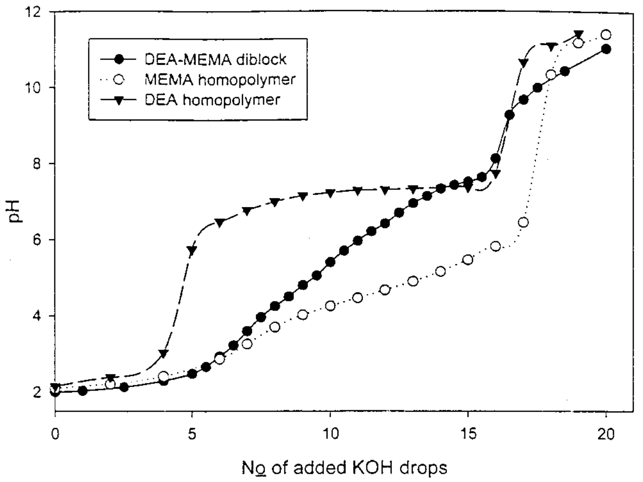

Figure 3. Titration curves obtained for the DEA homopolymer, the MEMA homopolymer, and the 40:60 DEA−MEMA diblock copolymer.

The titration curves (see Figure 3) for the DEA and MEMA homopolymers were obtained by dissolution (1.5×10^{-2} M, based on tertiary amine residues) at pH 2 and then monitoring of the pH as KOH solution (0.5−1.0 M) was gradually added. From these curves, the pK_a values were calculated to be 7.3 and 4.9 for the DEA and MEMA homopolymers, respectively.

The measured pK_a of 7.3 for the conjugate acid of DEA homopolymer agrees very well with the value reported by Lee et al.[20] DEA homopolymer was also expected to be more basic than MEMA homopolymer on the basis of the analogous small molecules.[21] For example, the pK_a of triethylamine is 10.98, which is much higher than that for morpholine (pK_a = 8.13).[22] Thus, the small molecule analogue of MEMA is considerably less basic than that of DEA. The same trend was also observed for the pK_a values of both of the DEA and MEMA monomers (8.9 and 6.1, respectively) and, more pertinently, for the pK_a's of their homopolymers (7.3 and 4.9, respectively).

MEMA homopolymer exhibits inverse temperature−solubility behavior, and its pK_a is 4.9, as discussed earlier. Thus, above pH 6, these chains are soluble in their nonprotonated, neutral form. Depending on molecular weight, the cloud-point of MEMA homopolymer ranges from 34 to 54 °C at pH 7−8.[18] Compared to most other water-soluble polymers, MEMA homopolymer can also easily be precipitated (salted out) from aqueous solution on addition of electrolytes such as Na_2SO_4, K_2CO_3, Na_3PO_4, and so on. On the other hand, DEA homopolymer dissolves as a cationic polyelectrolyte in acidic solution due to protonation of its tertiary amine residues. Precipitation from aqueous solution occurs when the solution pH exceeds the pK_a of 7.3 for DEA homopolymer, because the average degree of protonation drops below a critical value and the chains become hydrophobic. In contrast, MEMA homopolymer remains water soluble at room temperature in mildly alkaline media.

In view of these observations, we realized that the subtle variation of the hydrophilic/hydrophobic balance of these diblock copolymers provided a unique opportunity to prepare both DEA−core micelles and MEMA−core micelles from the same copolymer in aqueous solution (see Figure 1).

DEA−Core Block Copolymer Micelles. All three diblock copolymers dissolved molecularly in dilute HCl at pH 4. Careful addition of KOH to these acidic solutions at 20 °C produced a final pH of between 7.5 and 8.5, depending on the block compositions (see Table 1). Under these conditions, the DEA block is substantially deprotonated and therefore hydrophobic, whereas the MEMA block remains solvated. Thus, micelles comprising DEA cores and MEMA coronas are expected. Dynamic light scattering experiments (see Table 2) and ^1H NMR studies confirmed this to be the case.

The ^1H NMR spectrum in Figure 4 represents a 40:60 DEA−MEMA diblock copolymer (VB256A) in both $CDCl_3$ (Figure 4a) and D_2O (Figure 4b−d). By comparing parts b and c of Figure 4, it is clear that the signals due to the DEA residues at δ 1.3 and δ 3.3 are suppressed (indicating lower mobility and decreased solvation for this block), whereas signals due to the MEMA block at δ 2.6 and δ 3.7 are still prominent.

MEMA−Core Block Copolymer Micelles. ^1H NMR studies at 20 °C in D_2O at pH 6.7 in the presence of 1.0 M Na_2SO_4 confirmed that the DEA block remains solvated under these conditions (note the prominent signals at δ 1.3, 3.3, 3.5, and 4.4), whereas the signals due to the MEMA block at δ 2.6, 3.7, and 4.1 are suppressed (compare parts b and d of Figure 4). This is consistent with the MEMA block forming the nonsolvated micelle core, which is entirely expected given its low tolerance to added electrolyte. As expected, block symmetry is important for the formation of stable micelles and reverse micelles. Thus micellization studies with the more asymmetric 27:73 DEA−MEMA diblock copolymer were only partially successful: since the DEA block was relatively short, the long-term stability of the MEMA−core micelles was poor. Maintaining the solution temperature at or below 20 °C is also critical for

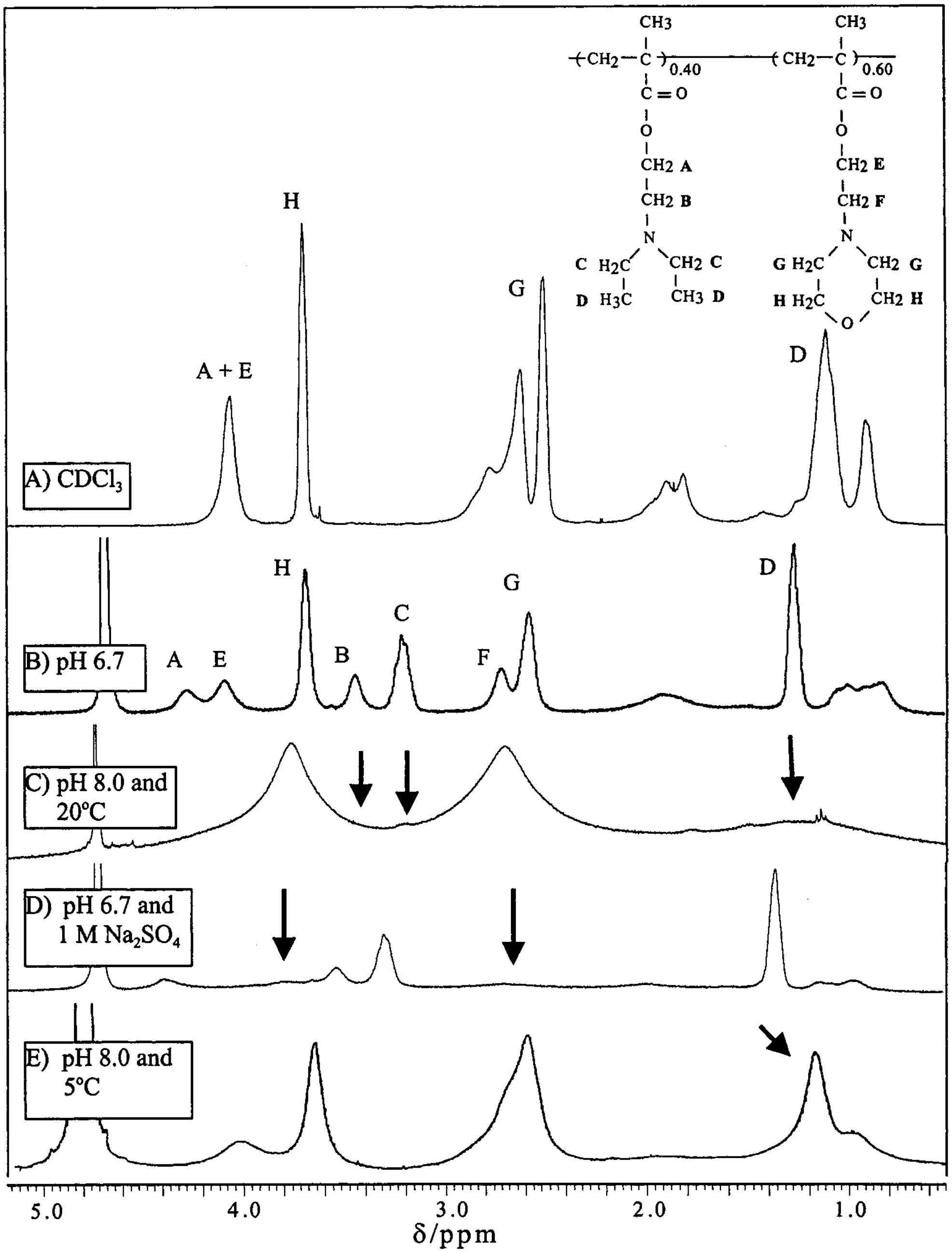

Figure 4. ^{1}H NMR spectra recorded for the 40:60 DEA–MEMA diblock copolymer obtained under the following conditions: (a) in $CDCl_3$ (a nonselective solvent, thus both block are solvated); (b) in D_2O at 20 °C and pH 6.7 (both DEA and MEMA blocks are solvated); (c) in D_2O at 20 °C and pH 8.0 (DEA–core micelles); (d) in D_2O at 20 °C and pH 6.7 in the presence of 1.0 M Na_2SO_4 (MEMA–core micelles); (e) in D_2O at 5 °C and pH 8 (resolvation of the DEA residues; compare to spectrum c).

the successful formation of DEA–core micelles (see Figure 4d): more polydisperse micelles or macroscopic precipitation was obtained at 25 °C or higher. However, it is noteworthy that, on cooling a solution of DEA–core micelles at pH 7–8 to 5 °C, the DEA chains became rehydrated (see Figure 4e), which suggests that micelle dissociation occurs. This is presumably because the cloud-point (LCST) of DEA homopolymer lies somewhere between 5 and 20 °C.

Dynamic/Static Light Scattering Studies. Dynamic light scattering studies indicated near-monodisperse micelles, with intensity-average micelle diameters of 21–35 nm at 20 °C and pH 8. Addition of acid led to reprotonation of the DEA residues, leading to the formation of unimers below pH 6.7 and 20 °C. By use of this unimer solution at pH 6.1–6.7, MEMA–core micelles were obtained by selective salting out of the MEMA block using 1.0 M Na_2SO_4. Careful control of the solution pH was essential. If the solution pH was too low, both of the DEA and MEMA blocks would become soluble as weak cationic polyelectrolytes. Conversely, if the solution pH was too high, the DEA block would become desolvated in addition to the MEMA block, and macroscopic precipitation would occur. A solution pH of 6.1 to 6.7 was found to be a suitable compromise. Both blocks are soluble under these conditions but, given the difference in pK_a values, the DEA block is protonated and the MEMA block is nonprotonated. Under these conditions, dynamic light scattering studies indicated the formation of colloidally stable, near-monodisperse, MEMA–core micelles, with intensity-average diameters of 26 nm for a 40:60 DEA–MEMA

Table 3. Weight-Average Molecular Weights, Hydrodynamic Diameters, Polydispersities, and Mean Aggregation Numbers of the Micelles and Reverse Micelles Formed by the 40:60 DEA–MEMA Diblock Copolymer (M_w = 27 300 by GPC) at 20 °C

				micelle diameter/nm		
solvent for SLS studies	Na_2SO_4 conc (M)	dn/dc[a]	M_w by SLS	DEA core[b] diam/(PD)	MEMA core[b] diam/(PD)	N_{agg}[c]
THF		0.096	30,000	unimers	unimers	1.1 ± 0.1
pH < 7	0.0			unimers	unimers	
pH 8	0.0	0.0125	2.2×10^6	33 (0.057)		74 ± 7
pH 6.5	1.0	0.0166	2.9×10^6		26 (0.022)	97 ± 9

[a] As determined using differential refractometry. [b] As determined on 1.0 w/v% copolymer solutions by DLS. [c] The aggregation number, N_{agg}, is calculated from the SLS data by dividing the M_w of the micelles formed by the 40:60 DEA–MEMA diblock copolymer in aqueous media by the M_w of 30 000 obtained for the same copolymer when molecularly dissolved in THF.

diblock and 29 nm for a 50:50 diblock (see Table 3). The slightly larger diameter in the second case is presumably due to the longer DEA chains leading to a thicker micelle corona.

SLS measurements were carried out for the 40:60 DEA–MEMA block copolymer solutions, and the results are summarized in Table 3. The weight-average molecular weight (M_w) of 30 000 found for this copolymer in THF is in very good agreement with the M_w of 27 300 obtained by GPC, especially given the possibly inappropriate PMMA calibration standards used in the latter technique. Even after allowing for experimental uncertainties, the M_w of the MEMA–core micelles is significantly higher than that for the corresponding DEA–core micelles.

The MEMA–core micelles have a mean aggregation number of 97 ± 9, whereas for the DEA–core micelles, the mean aggregation number is 74 ± 7. These differences are consistent with the block asymmetry and with the influence of corona-forming chains on the micelle structure.[5] Considering the dynamic and static light scattering data together, it appears that the smaller MEMA–core micelles are much more compact than the DEA–core micelles, which probably reflects the lower packing efficiency for the latter micelles.

Surface Tension Measurements by Surface Light Scattering. For chemically pure, low-molecular-weight surfactants, surface tension measurements are generally used to determine the critical micelle concentration (cmc) via a characteristic break-point in the surface tension versus ln c curve. Polymeric surfactants have molecular weight distributions rather than a unique molecular weight; thus, surface tension measurements generally result in a smooth curve and there is no well-defined cmc. This is because hydrophobicity depends on molecular weight. In view of the low polydispersity of our diblock copolymers, we studied the surface tension behavior from 1×10^{-4} to 1.0%, in an attempt to measure the cmc. The experiments were carried out at pH 8.5 where the DEA blocks are hydrophobic, in 1.0 M Na_2SO_4 at pH 6.5 where the MEMA block is hydrophobic, and at pH 2 where only unimers are present. The "background" surface tension depends on the solvent buffer, and for the high electrolyte concentration system, this is 2–3 mN m^{-1} higher than pure water (~72.8 mN m^{-1}). In all three cases, the surface tension decreased with copolymer concentration, indicating adsorption, but no clear cmc break points could be identified; this is presumably due to polydispersity effects, as outlined above. However, in the high concentration regime, a limiting surface tension was achieved, and the results obtained at 1.0 w/v % copolymer concentration make for an interesting comparison. For the unimer solution at pH 2, γ_0 is 42 mN m^{-1}, whereas both of the micellar solutions gave γ_0 values of approximately 33 mN m^{-1} (the experimental uncertainties are ±1 mN m^{-1}). These results suggest that the molecularly dissolved cationic unimers are less strongly adsorbed at the air–water interface, and the propensity for strong copolymer adsorption at the air–water interface is similar regardless of which block (DEA or MEMA) is made selectively hydrophobic (N.B., the absolute surface tension depends on both the extent of adsorption *and* the chemical nature of the hydrophobic chains[23]).

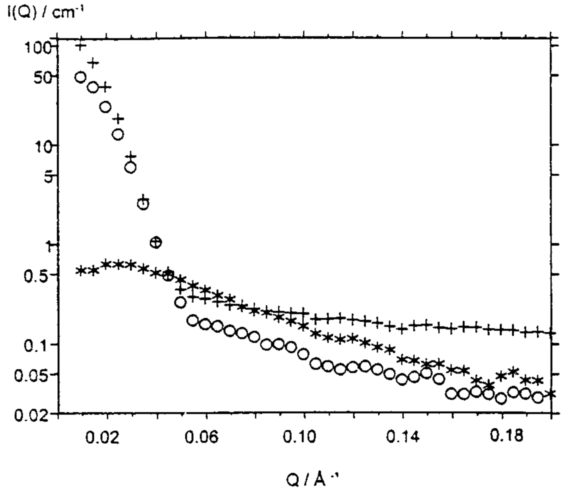

Figure 5. Typical SANS data for the 40:60 DEA–MEMA diblock copolymer (M_w 30 000) at ϕ = 0.0125, in D_2O as a function of pH: (+) DEA–core micelles at pH 8.5, 16 °C; (○) MEMA–core micelles at pH 6.5 in 1.0 M Na_2SO_4 at 20 °C; (*) unimers at pH 2 and 20 °C.

Small-Angle Neutron Scattering Studies. Unimer-to-Micelle Transition. Figure 5 shows three scattering curves for the 40:60 DEA–MEMA diblock copolymer (M_w = 30 000) corresponding to DEA–core micelles (at pH 8.5), MEMA–core micelles (at pH 6.5, 1.0 M Na_2SO_4) and a unimer solution (at pH 2) at a constant copolymer concentration of $\phi = 0.0125$, which was the most dilute case.

The effect of pH on the solution structure is clearly apparent. In acidic solution, the weak scattering is characteristic of a dilute molecular solution, whereas for the other two copolymer solutions, a 100- to 200-fold increase in intensity at low Q and steep decay of the signal indicate significant aggregation (micelle formation). Furthermore, given the slightly lower intensities and a small shift to high Q, at first sight it would appear that the MEMA–core micelles are slightly smaller than the DEA–core micelles. These general features were reproducible and were concentration-

Table 4. Fitted Parameters Obtained from Least-Squares Analyses of SANS Data for the Micelles Formed by the 40:60 DEA−MEMA Diblock Copolymer (M_w = 30 000) Using a Polydisperse Sphere Model[a]

micelle core	ϕ	Guinier D nm	Porod D nm	fit D_{av}* nm	sf* × 10^4 cm^{-1}	p*	D_{hs}* nm	V_{mic} × 10^{18} cm^3	N_{mic} × 10^{-16} cm^{-3}	N_{agg}
DEA	0.1	21.4	18.0	17.6	1.59	0.20	18.0	2.85	3.54	57
16 °C	0.05	25.2	21.6	20.7	0.76	0.19	20.0	4.66	1.03	98
	0.025	24.6	21.6	20.0	0.40	0.18	20.0	4.18	0.61	82
	0.0125	25.4	21.6	20.6	0.20	0.19	20.0	4.56	0.28	90
				(19.7)						(82)
MEMA	0.1		20.0	16.8	0.75	0.23	25.8	2.47	1.93	104
20 °C	0.05		18.6	15.0	0.37	0.23	25.6	1.79	1.32	76
	0.025	22.4	20.0	17.8	0.24	0.20	20.0	3.00	0.51	98
	0.0125	23.4	20.0	18.6	0.14	0.21	20.0	3.37	0.25	99
				(17.0)						(94)

[a] The parameters are the micelle diameter, D, scale factor, sf, hard-sphere diameter for $S(Q)$, D_{hs} (the hard-sphere volume fraction was fixed at that given by the total copolymer concentration). Fitted parameters are indicated by *, uncertainties in dimensions are ±0.2 nm, and the scale factor is ±5%. The micelle volume and number density are V_{mic} and N_{mic}, and N_{agg} is the aggregation number given by N_{pol}/N_{mic}. The average micelle diameter and mean aggregation number are given in parentheses.

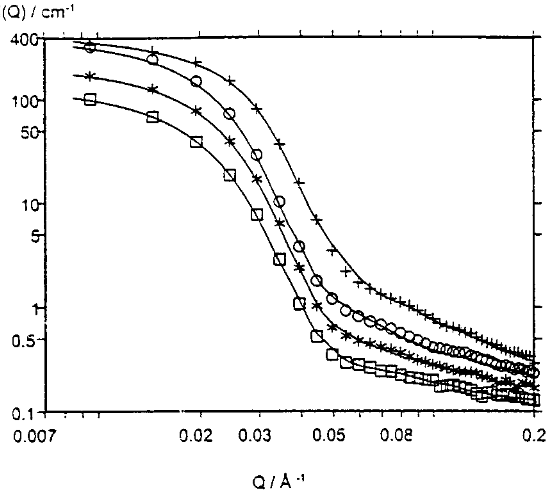

Figure 6. SANS data and fitted curves for the polydisperse sphere model for DEA−core micelles formed by the 40:60 DEA−MEMA diblock copolymer (M_w 30 000) in D_2O, at pH 8.5 and 16 °C, as a function of volume fraction. ϕ = 0.10 (+), 0.05 (○), 0.025 (*), and 0.0125 (□). The fit parameters are given in Table 4.

independent, at least in the concentration range studied (ϕ = 0.0125−0.10). Absolute intensities scaled directly with ϕ, suggesting that the micelle structure did not change over the concentration range investigated. Detailed analyses of these data were carried out, as described below.

Micellar Solutions. Figure 6 shows SANS data for DEA−core micelles at pH 8.5 at 16 °C as a function of volume fraction.

Clearly, the scattering intensity scales with concentration, but the Q-dependence does not change. Furthermore, the absence of any peak maxima suggests that interparticle interactions ($S(Q)$) are relatively weak. A similar family of curves was obtained, over the same concentration range, for MEMA−core aggregates at pH 6.5, 1.0 M Na_2SO_4, and 20 °C. Initial analyses were carried with the Guinier law (eq 1): all of the data gave reasonably linear regions at low Q (<0.04 Å^{-1}), and mean micelle diameters were estimated from least-squares fits in this region. Although the lowest Q-points satisfy the Guinier condition (QR < 1), diameters were also obtained from peak maxima on Porod plots ($I(Q)$-Q^4 vs Q) as described in the Experimental Section. This method uses data at high Q (Q_{max} ~ 0.22 Å^{-1}), which is helpful if insufficient points are available in the low Q (Guinier) range. Table 4 quotes micelle diameters obtained from these analyses (these are denoted D to distinguish from the hydrodynamic diameter d determined by DLS). There is reasonable agreement between the two approaches: the DEA−core micelles and MEMA−core aggregates are of similar size (for the highest copolymer concentrations with MEMA−core micelles, the Guinier analysis was less reliable owing to $S(Q)$; see discussion below).

More detailed structural information can be obtained from fitting the scattering data with models using the FISH software[11] to test various structures. Since the Guinier analysis was consistent with spherical aggregates, the following models were tested with, and without, hard-sphere or repulsive electrostatic $S(Q)$: monodisperse spheres, polydisperse spheres (Schultz, concave, spike distributions), monodisperse and polydisperse (Schultz) core−shell particles (i.e., accounting for a well-defined corona of scattering length density ρ_{shell} and thickness t), and finally ellipsoids. The criteria for selecting the best model were (a) minimum χ^2 and (b) agreement between fitted scale factor (sf) and that based on the known copolymer structure. Of all these possibilities, a Schultz polydisperse sphere form factor with a hard-sphere structure factor met these two conditions best (especially b): fitted lines for this model are shown in Figure 6. Surprisingly, the core−shell form factor did not fit well, since this scattering law necessarily results in a minimum at high Q,[23] a feature which is absent from these measured data (see Figure 6). The minimum disappears when the neutron scattering contrast between core and shell is reduced, but under these conditions, the scattering law reduces to that of a homogeneous sphere.[23] Therefore, it may be concluded there is insufficient neutron contrast to highlight the coronal shell of these DEA−MEMA micelles. This might be expected given the similar isotopic composition of the two tertiary amine methacrylate blocks (Figure 1) and in the absence of strong preferential solvation of the outer shell. In other words, the transition from core to corona is too diffuse and ill-defined in terms of neutron scattering length density; as far as the neutron scattering data is concerned, the main boundary is between the hydrocarbon-based micelles and the surrounding D_2O. To determine the separate DEA and MEMA shell thicknesses, it would be necessary to selectively deuterate one of the blocks. Fitted parameters in the final analyses were the scale factor sf, average micelle

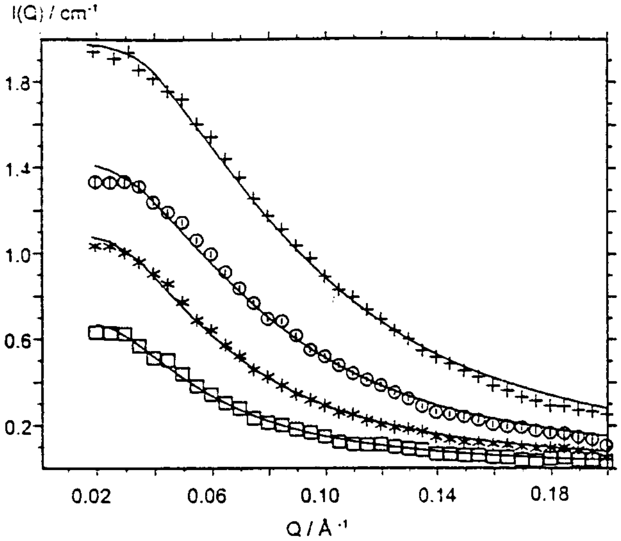

Figure 7. SANS data and fitted curves for the Gaussian coil model as a function of volume fraction for unimer solutions of the 40:60 DEA−MEMA diblock (M_w 30 000) in D_2O at pH 2 and 20 °C. $\phi = 0.10$ (+), 0.05 (○), 0.025 (*), and 0.0125 (□). The fit parameters are given in Table 5. Representative error bars are given for the $\phi = 0.05$ data.

diameter D_{av}, polydispersity index *p*, and effective hard-sphere diameter D_{hs}: Table 4 lists these values.

For both types of micelles, the fitted mean diameter is slightly smaller that those obtained from Guinier and Porod approximations. In all cases, the diameters determined from SANS are smaller than those obtained by DLS (Table 3). This is to be expected since the latter value includes hydration, whereas neutrons are only sensitive to (sharp) changes in scattering length density, which occur at the micelle periphery where D_2O gives way to hydrocarbon polymer. By comparing the fitted diameters of the two micelles, it is clear that DEA−core micelles are larger than the corresponding MEMA−core micelles (mean values given in parentheses in Table 4 are 19.7 and 17.0 nm, respectively). Similar size differences were observed by DLS (see Table 3: 33 vs 26 nm). As exemplified by the high *Q* data, there is a significant polydispersity owing to the absence of a form factor minimum. This is reflected in the fitted polydispersity index *p* which is around 0.20 (i.e., 20%), as typically found for micelles and microemulsions in aqueous media.[13,24] Values for the effective micelle volume V_{mic} are based on the average particle diameter and polydispersity, and in combination with fitted scale factors can be used to estimate micelle number densities N_{mic}. Hence, assuming all the polymer is aggregated (i.e., a very low cmc), the apparent aggregation number N_{agg} may be obtained. This analysis leads to mean N_{agg} values of 82 and 94 (see Table 4) for the DEA−core micelles and MEMA−core micelles, respectively. These values compare favorably with those obtained from static light scattering, which are 74 and 97, respectively (see Table 3). Hence, the SANS and static light scattering measurements are consistent in that the two types of micelles have similar structures and aggregation numbers. This agreement reinforces the hypothesis that the MEMA−core micelles form denser, more compact aggregates than those of the relatively loosely packed DEA−core micelles.

Unimer Solutions. Figure 7 shows SANS curves as a function of copolymer concentration for the unimer solutions at pH 2. As stated earlier, the scattering intensities are much lower than those for the micellar solutions; however, there is a clear scaling relationship with ϕ. In view of the polyelectrolytic nature of these DEA−MEMA diblock copolymers in strongly acidic media, scattering characterized by repulsive interactions was expected. However, in the accessible *Q*-range there was only a smooth decay, with no evidence for any peaks; this decay could be fitted by the simple Gaussian coil model describing a swollen, noninteracting chain in a ϑ solvent. The fits are shown in Figure 7, and calculated parameters are listed in Table 5. The scale factor *I(0)* can be used to estimate the molecular weight, resulting in values between a factor of 1.8 and 5.2 higher than that found by static light scattering in THF solvent (Table 3). This apparent discrepancy can be reconciled if hydration effects are considered: association of D_2O with the copolymer will reduce the effective contrast term ($b_1 - b_2\bar{V}_1/\bar{V}_2$), hence giving rise to a lower apparent molecular weight. By use of this approach, an effective hydration number of between 19 and 30 can account for the SANS intensities obtained for the 40:60 DEA−MEMA diblock polymer.

Table 5. Results from Least-Squares Analyses of SANS Data, with eq 3, for the 40:60 DEA−MEMA Diblock Copolymer Solutions at pH 2[a]

ϕ	*I(0)** cm^{-1}	R_g* nm	$N_{pol} \times 10^{-18}$ cm^{-3}	M_w g mol^{-1}	SANS M_w/LS M_w
0.1	2.22	1.93	2.01	156 786	5.2
0.05	1.58	2.22	1.00	110 147	3.7
0.025	1.26	2.77	0.50	69 060	2.3
0.0125	0.82	3.14	0.25	53 059	1.8

[a] The parameters are *I(0)* the fitted absolute scale factor (given by the pre-exponential term in brackets in eq 3), R_g is the radius of gyration, and N_{pol} is the number density of copolymer chains. Fitted parameters are indicated by *, uncertainties in R_g are ±0.2 nm, and *I(0)* is ±5%. M_w was obtained from the fitted *I(0)* assuming no hydration. The new contrast factor accounts for copolymer−D_2O hydration, resulting in estimates for the hydration number n_{hyd}, and the effective number of water molecules associated with each copolymer segment.

Although at first sight, this random coil-based interpretation may seem naïve, the SANS data from copolymer solutions at pH 2 are consistent with dilute, nonaggregated DEA−MEMA chains, i.e., unimers. If a moderate degree of solvation is allowed for, the SANS data can be interpreted in terms of a simple model which is consistent with the M_w values obtained from static light scattering.

Conclusions

In summary, a new class of DEA−MEMA diblock copolymers can form micelles with nonsolvated cores comprising either the DEA block or the MEMA block in aqueous media at 20 °C. In both cases, micellization is fully reversible. It is remarkable that this highly unusual behavior can be observed at room temperature merely by judicious control of the solution pH and the electrolyte concentration. Surface tension measurements obtained from surface light scattering studies show that strong copolymer adsorption occurs at the air−water interface if either of the two blocks is rendered hydrophobic. Given the approximations involved, the SLS and SANS data are in reasonable agreement for the 40:60 DEA−MEMA diblock copolymer. In particular, both methods indicate a distinct increase in mean micelle diameter and decrease in mean aggregation number for the DEA−core micelles compared to the MEMA−core micelles. This indicates that the MEMA−core micelles are more compact than the DEA−core micelles, which is presumably related to the block asymmetry. For unimer solutions, the SANS and SLS data can be reconciled if weak hydration of the polymer chains is invoked.

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