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Effect of Partial Quaternization on the Aqueous Solution Properties of Tertiary Amine-Based Polymeric Surfactants: Unexpected Separation of Surface Activity and Cloud Point Behavior

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Introduction. 2-(Dimethylamino)ethyl methacrylate (DMA) is an interesting hydrophilic monomer, with potential applications in textiles, pigment dispersion, hydrogels, and synthetic vectors for DNA complexation.[1] Cationic copolymers based on quaternized DMA monomer are widely used to treat industrial and municipal effluent waste and also as retention aids in the papermaking industry.[2] DMA homopolymer is soluble in aqueous media at low pH as a weak cationic polyelectrolyte ($pK_a = 7.0 \pm 0.5$[3]) due to protonation of the tertiary amine groups. At pH 8 or above, DMA homopolymer has very low or zero charge density, and hydrogen bonding is solely responsible for its water solubility. Under these conditions, the neutral DMA chains exhibit inverse temperature solubility, and the observed LCST (or cloud point) depends on the degree of polymerization.[4] Since DMA monomer has no labile protons, it is amenable to group transfer polymerization (GTP), which leads to narrow molecular weight distributions and the possibility of well-defined DMA-based block copolymers via sequential monomer addition. In recent years we have prepared a wide range of controlled-structure DMA-based copolymers via GTP.[4−8] In particular, diblock copolymers based on DMA and the closely related monomer, 2-(diethylamino)ethyl methacrylate (DEA), were shown to be interesting pH-responsive polymeric surfactants,[7,8] which exhibit strong surface activity and form well-defined micelles (with the DEA block located in the core and the DMA block in the corona) in aqueous solution at pH 7−8. However, above pH 8, precipitation of these micelles occurs due to deprotonation of the DMA residues. The DMA residues in DMA−DEA diblock copolymers can be fully and selectively quaternized using methyl iodide, provided that a stoichiometric amount of the alkyl halide is utilized under mild conditions.[9] This derivatization increases the hydrophilicity of the DMA block significantly (LCST behavior is no longer observed) and substantially extends the pH range over which the quaternized copolymer micelles are soluble. Unfortunately, the surface activity of these fully quaternized diblocks is compromised, presumably due to strong, lateral electrostatic repulsion between the highly cationic DMA chains. (The DEA chains are hydrophobic and hence are adsorbed at the air−water interface.)

Herein we demonstrate that *low* degrees of quaternization (approximately 10 mol %) of the DMA block are sufficient to eliminate LCST behavior. Moreover, these lightly quaternized diblocks exhibit surprisingly high surface activities, which are comparable to that found for the corresponding DMA−DEA diblock precursor.[10] Thus, lightly quaternized DMA−DEA diblock copolymers are robust, powerful surfactants with a wide range of potential applications as dispersants, emulsifiers, and stabilizers.

Experimental Section. A DMA homopolymer ($M_n = 5350$; $M_w/M_n = 1.12$ using THF GPC and PMMA standards) and a DMA−DEA diblock copolymer (75 mol % DMA by ^{1}H NMR; $M_n = 8200$; $M_w/M_n = 1.10$) were synthesized by GTP as described previously.[7,11] Absolute M_n values were determined by end group analysis using ^{1}H NMR spectroscopy (300 MHz Bruker instrument; $CDCl_3$) by comparing the methoxy protons due to the

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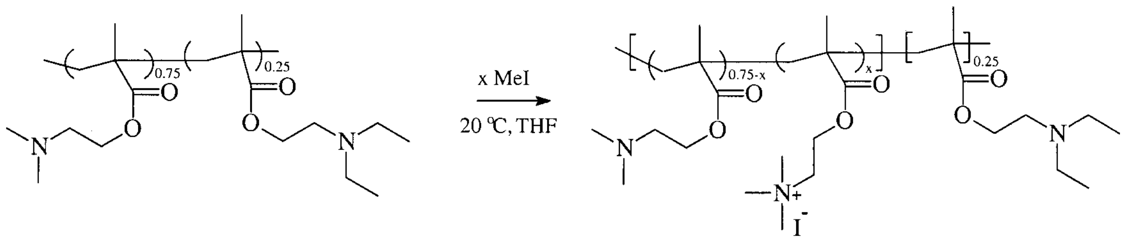

M_n = 8,200; M_w/M_n = 1.10

Figure 1. Reaction scheme illustrating the selective quaternization of the DMA residues in a DMA–DEA diblock copolymer using methyl iodide under mild conditions. The DEA residues are more sterically congested and hence remain unquaternized.

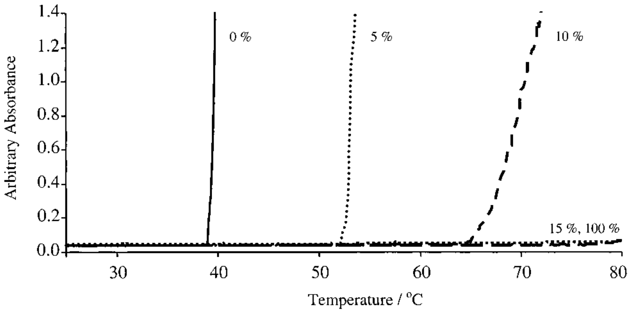

Figure 2. Turbidimetry vs temperature curves obtained at pH 8.8 for 1.0% w/v aqueous solutions of the DMA homopolymer at varying levels of quaternization. The cloud points were determined from tangents constructed from the turbidimetry curves.

silyl ketene acetal GTP initiator at δ 3.6 to those due to the dimethylamino protons at δ 2.4, as described previously.[4] Quaternization of the DMA residues in each polymer was achieved using methyl iodide in THF at 20 °C, as described by Bütün et al.[9,11] ^{1}H NMR was also used to determine the degree of quaternization: the integral of the trimethylammonium signal at δ 3.3 was compared to that of the oxymethylene signal at δ 4.1, as described previously.[9] Turbidimetry studies were performed using a Perkin-Elmer Lambda 2S spectrophotometer, and surface tension data were recorded using a Krüss K10 tensiometer operating at 20 °C.

Results and Discussion. Target degrees of quaternization were readily achieved by adjusting the molar ratio of methyl iodide to DMA residues for both the DMA homopolymer and the DMA–DEA diblock copolymer, as expected. In the case of the diblock copolymer (see Figure 1), quaternization was selective provided that mild conditions were employed, and the methyl iodide was used in (sub)stoichiometric quantities relative to the DMA residues. This is because the DEA residues are more sterically congested, and hence less reactive, than the DMA residues.[9]

Several turbidimetry curves are depicted in Figure 2. It is clear that increasing the degree of quaternization of the DMA homopolymer leads to marked elevation of the cloud point. The unquaternized precursor exhibits a cloud point at 39.3 °C in dilute aqueous solution at pH 8.8, which is consistent with the cloud point vs M_n relationship previously observed by Bütün et al.[9] At degrees of quaternization of 5% and 10%, the cloud point shifts to 52.8 and 66.3 °C, respectively. No cloud point behavior is observed up to 100 °C for both the 15% and also the fully quaternized DMA homopolymer. A similar trend is found for the DMA–DEA diblock copolymer. In this case only 10% quaternization is sufficient to completely eliminate inverse temperature–solubility behavior. In view of the hydrophobicity of the DEA component, we had expected that the DMA–DEA diblock would require a higher (rather than lower) degree of quaternization than the DMA homopolymer in order to raise its cloud point above 100 °C. Presumably, the spherical micelles formed by the partially quaternized DMA–DEA diblock at pH 8.8 have a higher cationic charge density (and hence are more hydrophilic) than the partially quaternized random coils adopted by the DMA homopolymer chains under the same conditions.

Table 1. Effect of Degree of Quaternization on Cloud Points and Limiting Surface Tensions of 1.0% w/v Aqueous Solutions of the DMA Homopolymer and DMA–DEA Diblock Copolymer at pH 8.8 and 20 °C

polymer type	deg of quaternization by ^{1}H NMR[c]/ mol %	limiting surf. tension[d]/ mN m^{-1}	cloud point[d]/°C
DMA homopolymer[a]	0	48.1	39.3
	5	48.1	52.8
	11	49.5	66.3
	15	50.3	>100
	100	64.0	>100
DMA–DEA diblock copolymer[b]	0	34.6	36.9
	9	37.5	>100
	19	37.8	>100
	100	51.3	>100

[a] M_n = 5350, as determined by ^{1}H NMR using the GTP initiator as an end group. [b] M_n = 8200, as determined by ^{1}H NMR using the GTP initiator fragment as an end group. [c] As determined by ^{1}H NMR (see text). [d] Determined on 1.0% w/v aqueous solutions at pH 8.7–8.8 and 20 °C.

Table 1 summarizes the effect of varying the degree of quaternization on the cloud points (LCST) and the limiting surface tensions (1.0% w/v aqueous solutions at pH 8.8) of the DMA homopolymer and the DMA–DEA diblock copolymer. It is obvious that, in both cases, increasing the degree of quaternization elevates the cloud point dramatically but at the same time suppresses surface activity. The latter trend is more readily discernible if the pH dependence of the surface tension is examined.

Figure 3 depicts surface tension vs pH curves for the unquaternized DMA–DEA diblock copolymer and also for the same copolymer after quaternization with 10, 20, and 100 mol % methyl iodide. At low pH all residues (both DMA and DEA) are either quaternized or protonated, and the highly cationic copolymer chains have very low surface activities (and correspondingly high surface tensions of 60–66 mN m^{-1}). As the solution pH is increased, the protonated DMA residues become deprotonated, but the quaternized DMA residues remain cationic. For the diblock copolymer precursor, this means that micelles of very low charge density (hydrophobic DEA cores, near-neutral DMA coronas[8]) are

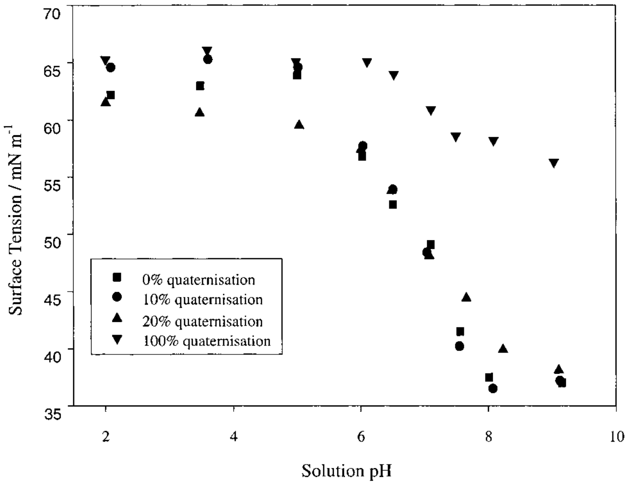

Figure 3. Surface tension vs pH curves for 0.50% w/v aqueous solutions of the DMA−DEA diblock copolymer at 20 °C as a function of quaternization.

formed between pH 7 and pH 8. In more alkaline solution (pH 9.3) the neutral DMA coronas are no longer hydrophilic, and precipitation occurs at 20 °C. The 10% and 20% quaternized diblock copolymers exhibit very similar surface vs pH curves to the unquaternized precursor *but remain soluble up to pH 14*. Surface tensions are as low as 37−38 mN m^{-1}, and these aqueous solutions form highly stable foams on agitation. In contrast, the fully quaternized DMA−DEA diblock copolymer is only very weakly surface active between pH 7 and pH 9, with surface tension values remaining above 56−58 mN m^{-1}.

Conclusions. In summary, it is shown that low degrees of quaternization eliminate the LCST behavior of DMA−DEA diblock copolymers and significantly extend the pH (and temperature) range for colloidally stable micelles. Similar results were previously reported for fully quaternized DMA−DEA diblock copolymers, but these latter materials are very poor surfactants since unfavorable electrostatic interactions lead to poor packing efficiencies at the air−water interface. In contrast, in the present study it is shown that lightly quaternized diblock copolymers exhibit similar surface activities to the unquaternized diblock copolymer precursor; thus, judicious control of the degree of quaternization unexpectedly allows fine-tuning and optimization of the aqueous solution properties of these new cationic polymeric surfactants. We have already exploited these subtle effects in the synthesis of shell cross-linked micelles.[11,12]

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References and Notes

(1) (a) Creutz, S.; Jerome, R.; Kaptijn, G. M. P.; van der Werf, A. W.; Akkerman, J. M. *J. Coat. Technol.* **1998**, *70*, 41−46. (b) Creutz, S.; Jerome, R. *Prog. Org. Coat.* **2000**, *40*, 21−29. (c) Sassi, A. P.; Blanch, H. W.; Prausnitz, J. M. *J. Appl. Polym. Sci.* **1996**, *59*, 1337−1346. (d) Rungsardthong, U.; Deshpande, M.; Bailey, L.; Vamvavaki, M.; Armes, S. P.; Garnett, M. C.; Stolnik, S. *J. Controlled Release* **2001**, *73*, 359−380.

(2) Hoover, M. F. *J. Macromol. Sci., Chem.* **1970**, *A4*, 1327−1417.

(3) (a) Pradny, M.; Seveik, S. *Makromol. Chem.* **1985**, *186*, 111−121. (b) Merle, Y. *J. Phys. Chem.* **1987**, *91*, 3092−3098.

(4) Bütün, V.; Armes, S. P.; Billingham, N. C. *Polymer* **2001**, *42*, 5993−6008.

(5) Baines, F. L.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1996**, *29*, 3416−3420.

(6) (a) Lowe, A. B.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1998**, *31*, 5991−5998. (b) Bütün, V.; Lowe, A. B.; Armes, S. P.; Billingham, N. C. *J. Am. Chem. Soc.* **1999**, *121*, 4288−4289.

(7) Bütün, V.; Armes, S. P.; Billingham, N. C. *Chem. Commun.* **1997**, 671−672.

(8) Lee, A. S.; Gast, A. P.; Bütün, V.; Armes, S. P. *Macromolecules* **1999**, *32*, 4302−4310.

(9) Bütün, V.; Armes, S. P.; Billingham, N. C. *Macromolecules* **2001**, *34*, 1148−1160.

(10) Although we have focused on DMA−DEA diblock copolymers in this study, we have also observed very similar trends with DMA-based triblock copolymers. See: Unali, G.-F. PhD Thesis, University of Sussex, UK, 2001.

(11) Bütün, V. PhD Thesis, University of Sussex, UK, 1999.

(12) Bütün, V.; Armes, S. P.; Billingham, N. C. *J. Am. Chem. Soc.* **1998**, *120*, 12135−12136.

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