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Selective Quaternization of 2-(Dimethylamino)ethyl Methacrylate Residues in Tertiary Amine Methacrylate Diblock Copolymers

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ABSTRACT: 2-(Dimethylamino)ethyl methacrylate (DMA) was block copolymerized in turn with three other tertiary amine methacrylate comonomers, namely, 2-(diethylamino)ethyl methacrylate (DEA), 2-(diisopropylamino)ethyl methacrylate (DPA), and 2-(*N*-morpholino)ethyl methacrylate (MEMA), using group transfer polymerization. The DMA residues of each of these diblock copolymers were *selectively* quaternized using both methyl iodide and benzyl chloride under mild conditions to yield a series of novel cationic diblock copolymers that exhibit reversible pH-, salt-, and temperature-induced micellization in aqueous media.

Introduction

Poly[2-(dimethylamino)ethyl methacrylate] is a weak polybase that is soluble in aqueous media because of protonation of its tertiary amine groups. Recently, several research groups described the synthesis of well-defined, near-monodisperse (co)polymers based on 2-(dimethylamino)ethyl methacrylate (DMA) via various living polymerization techniques.[1−7] For example, Hoogeveen et al. described the synthesis and adsorption behavior of a range of diblock copolymers comprising DMA and 2,3-dihydroxypropyl methacrylate (DHPM).[1] These copolymers were prepared via classical anionic polymerization using protecting group chemistry for the DHPM residues. The same workers also reported the use of such copolymers as stabilizers and flocculants for oxide particles[2] and compared the adsorption of DMA and quaternized DMA homopolymers onto colloidal silica and titania particles.[3] Creutz et al. also described the controlled polymerization of DMA using classical anionic techniques. Zwitterionic diblock and triblock copolymers comprising DMA and sodium methacrylate were also prepared, using *tert*-butyl methacrylate as a protected monomer for the sodium methacrylate residues.[5] The related DMA−ammonium methacrylate diblock copolymers were claimed to have potential as universal pigment dispersants because a range of inorganic oxides and organic dyes could be readily dispersed in aqueous media over a wide pH range.[6,7] This behavior was attributed to the ubiquitous adsorption characteristics imparted by the DMA residues. Finally, Matyjaszewski and co-workers polymerized DMA via atom transfer radical polymerization (ATRP) to obtain well-defined homopolymers, diblock copolymers, and triblock copolymers.[8,9]

At Sussex we have had a long-standing interest in water-soluble block copolymers, particularly those based on DMA. In our initial studies we prepared a series of DMA−methyl methacrylate diblock copolymers[10] by group transfer polymerization (GTP) and examined their efficacy as steric stabilizers for the dispersion polymerization of styrene in alcoholic media.[11] The micellization behavior of these hydrophilic−hydrophobic diblock copolymers in aqueous solution was studied using both static and dynamic light scattering and analytical ultracentrifugation.[12] Thomas' group recently published a series of neutron reflectivity studies of our selectively deuterated DMA−methyl methacrylate copolymers adsorbed at the air−water interface.[13−16]

More recently, we focused on the synthesis and characterization of hydrophilic−hydrophilic, rather than hydrophilic−hydrophobic, block copolymers. For example, we described[17,18] the block copolymerization of DMA with 2-(diethylamino)ethyl methacrylate (DEA) by GTP. These copolymers exhibit strong pH-dependent surface activity and can form well-defined micelles in aqueous solution. A detailed study of the pH-induced micellization of one of our DMA−DEA copolymers was recently reported by Lee and co-workers.[19]

In earlier work we demonstrated that near-monodisperse DMA homopolymers[20.21] and DMA−alkyl methacrylate block copolymers[22] can be quantitatively quaternized under unexpectedly mild conditions using 1,3-propanesultone to produce a range of novel polysulfopropylbetaines. In a later paper[23] the remarkable *selectivity* of this reagent was also demonstrated. Thus, the DMA residues of a DMA−DEA diblock copolymer could be derivatized exclusively, provided that the reaction was carried out under mild conditions using a stoichiometric amount of the 1,3-propanesultone (although the DEA residues are more basic than the DMA residues, they are actually much less reactive because of steric hindrance). In the present work the DMA residues, in a range of tertiary amine methacrylate-based diblock copolymers, were selectively quaternized using more conventional quaternizing agents, namely, methyl iodide and benzyl chloride (see Figure 1).

The aqueous solubility, surface activity, and micellization behavior of the resulting cationic diblock copolymers was studied using turbidimetry, surface tensiometry, ^{1}H NMR spectroscopy, and dynamic light scattering, respectively.

Polymer Synthesis

Synthesis of Tertiary Amine Methacrylate Precursor (Co)polymers. All homopolymers and block copolymers were synthesized using group transfer polymerization (GTP) as described previously.[17,18] DMA monomer was always poly-

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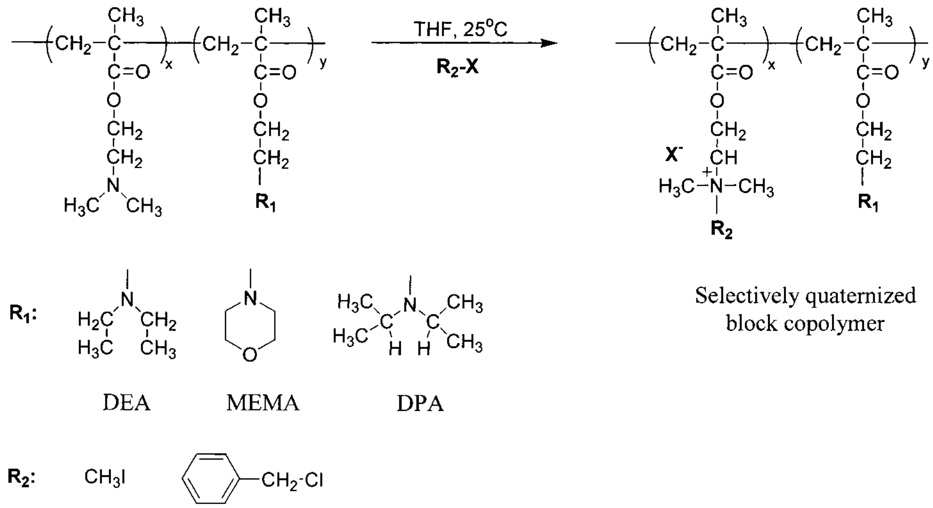

Figure 1. Reaction scheme for the selective quaternization of the 2-(dimethylamino)ethyl methacrylate residues in the tertiary amine methacrylate diblock copolymers.

Table 1. Number-Average Molecular Weights, Degree of Quaternization, Observed Precipitation Time, and Reaction Conditions of Four Tertiary Amine Methacrylate Homopolymers (Quaternization Was Carried Out Using Both MeI and BzCl, Respectively)

sample code[c]	polymer	precursor M_n[a] (g mol^{-1})	calcd. M_n[b] (g mol $^{-1}$)	solvent	precipitation time	reaction conditions	degree of quaternization (mol %)
VB128	Me−DMA	4000	7600	THF	10 min	25 °C, 24 h	100
VB133	Me−DMA	4750	9050	H_2O	soluble	25 °C, 24 h	100
VB130	Me−MEMA	12100	20700	THF	6 h	25 °C, 24 h	100
VB135	Me−MEMA	12100	20700	H_2O	soluble	25 °C, 24 h	100
VB131	Me−DPA	4800		THF		25 °C, 24 h	0
VB131	Me−DPA	4800	6900	THF	24 h	45 °C, 48 h	65
VB144	Me−DPA	4800	8000	THF	24 h	45 °C, 144 h	100
VB129	Me−DEA	11000	19450	THF	1 h	25 °C, 24 h	100
VB141	Bz−DMA	4750	8600	THF	3 h	65 °C, 48 h	100
VB142	Bz-DEA	3550		THF		65 °C, 48 h	5−10
VB143	Bz−MEMA	12100		THF		65 °C, 48 h	0

[a] As determined by GPC (calibrated with poly(methyl methacrylate) standards). [b] As calculated from GPC results of precursor homopolymers. [c] As determined by ^1H NMR spectroscopy.

merized first, followed by the addition of DEA, DPA, or MEMA, respectively.

Quaternization of the Tertiary Amine Methacrylate Homopolymers. Quaternization of each of the homopolymers was carried out using either methyl iodide (MeI) at 20 °C or benzyl chloride (BzCl) at 65 °C. In each case the alkyl halide/DMA molar ratio was 2.0. Homopolymer (2.0 g) was dissolved in either water or THF (40 mL) and the alkyl halide was added to this solution at the appropriate reaction temperature. Methylation of the DMA homopolymer was very fast and was complete within 10−20 min at 20 °C in both THF and H_2O. However, quantitative methylation of DEA homopolymer required 2−3 h in THF, and MEMA homopolymer required ≈10 h under the same conditions. Quaternization of DPA homopolymer with MeI was complete after refluxing in THF for 4−6 days. In contrast, benzylation of the DMA homopolymer required at least 1 day at reflux in THF. Because the resulting quaternized homopolymers were all insoluble in THF, excess quaternizing agent was readily removed by Soxhlet extraction. All four homopolymers were successfully methylated in THF. In addition, the hydrophilic DMA and MEMA homopolymers were also quaternized in aqueous media using MeI. The extent of quaternization was assessed by ^1H NMR spectroscopy.

Selective Quaternization of the DMA Residues in the Block Copolymers. Selective quaternization of the DMA residues in the DMA−DEA, DMA−DPA, and DMA−MEMA diblock copolymers (1−2 g) was carried out using a stoichiometric amount of MeI (based on the DMA content of the individual block copolymer) in THF at 25 °C for up to 24 h. Benzylation required refluxing THF for up to 48 h. Copolymers were usually purified by Soxhlet extraction with THF to remove excess quaternizing reagent. However, in the case of the selectively quaternized DMA−MEMA diblock copolymer, purification was achieved simply by precipitation in *n*-hexane. The resulting selectively methylated diblock copolymer was dried in a vacuum oven at 55 °C for 48 h. The extent of quaternization was assessed by ^1H NMR spectroscopy.

Quaternization of Selectively Betainized Diblock Copolymers. First, the DMA residues DMA−DEA, DMA−MEMA, or DMA−DPA diblock copolymers were selectively betainized using 1,3-propanesultone in THF at 20 °C, as reported in an earlier communication.[23] Then, the remaining DEA, MEMA, or DPA residues were successfully quaternized with methyl iodide in aqueous media. Typically, the selectively betainized block copolymer (1−2 g) was dissolved in deionized water (pH 6−7) in a single-necked 100-mL flask. Excess MeI (molar ratio of MeI to tertiary amine residues in the second block = 2.0) was then added via syringe and the aqueous solution was stirred for 1−4 days at 20 °C, depending on the nature of the second block. The resulting betainized/quaternized block copolymer was precipitated from aqueous solution into THF to remove excess unreacted MeI.

Polymer Characterization

Gel Permeation Chromatography. Molecular weights and molecular weight distributions of all precursor (co)polymers were determined using gel permeation chromatography (GPC). The GPC setup consisted of a Perkin-Elmer LC pump and a RI detector, the columns used were either Mixed "E" or Mixed "D" (Polymer Labs), and calibration was carried out using PMMA standards (Polymer Labs). The GPC eluent was HPLC-grade THF stabilized with BHT, at a flow rate of 1.0 mL min^{-1}. Molecular weights of the selectively quaternized diblock copolymers were calculated assuming 100% quaternization.

Nuclear Magnetic Resonance Spectroscopy (NMR). The compositions of all precursor block copolymers and the

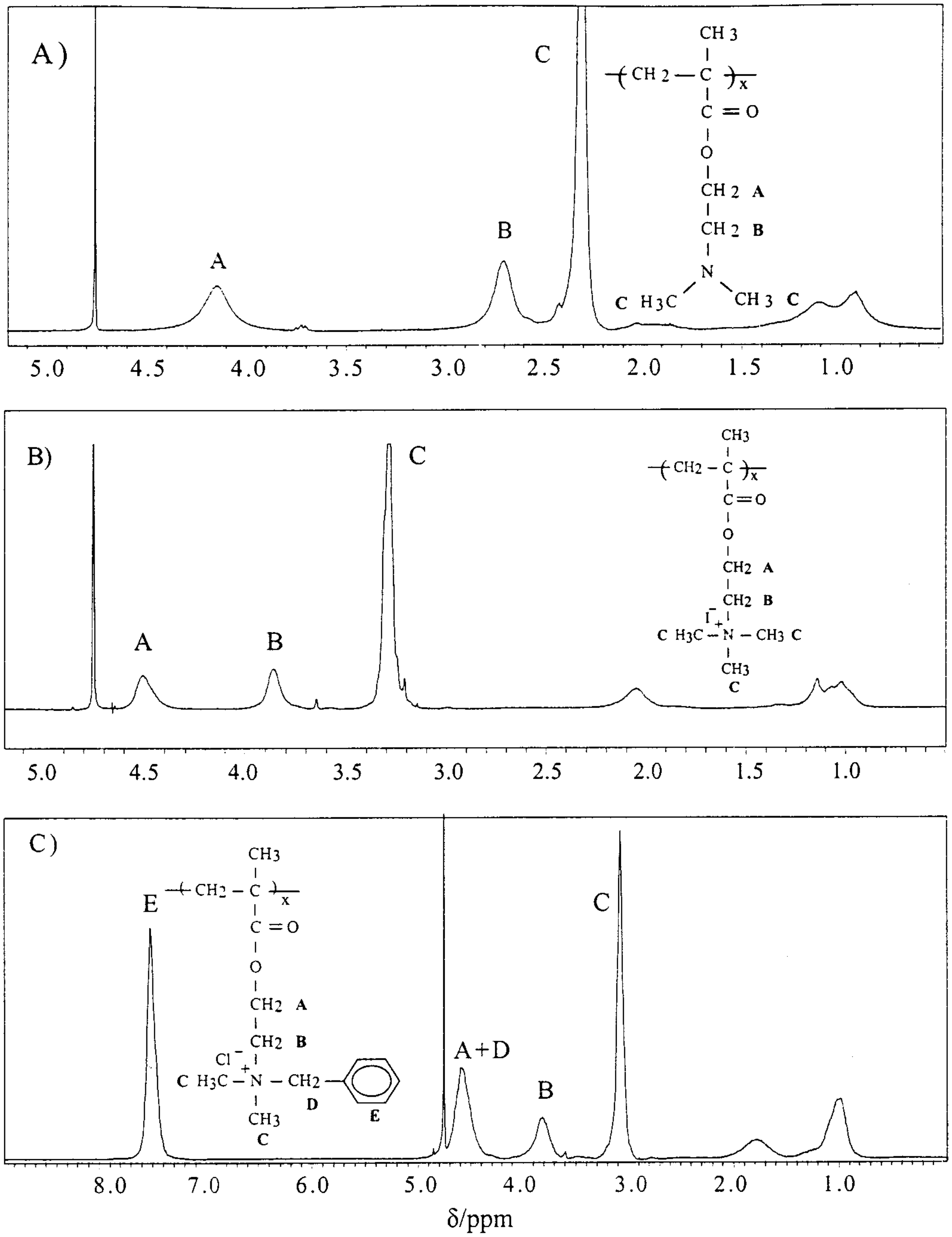

Figure 2. ^{1}H NMR spectra in D_2O of (a) DMA homopolymer, (b) methylated DMA homopolymer, and (c) benzylated DMA homopolymer.

micellization behavior of the selectively quaternized diblock copolymers in aqueous solution were investigated using either a Bruker AC-P 250- or 300-MHz instrument in D_2O/NaOD and D_2O/DCl. The degree of quaternization was also determined by comparing the peak integrals assigned to the different comonomers, before and after quaternization.

Dynamic Light Scattering Studies (DLS). The hydrodynamic size of the selectively quaternized block copolymer micelles in aqueous solution was measured using a Malvern 4700 dynamic light scattering instrument equipped with an 80-mW argon ion laser operating at $\lambda_0 = 632.8$ 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 1.0 w/v % solutions. The solution temperature was controlled to within ±0.1 °C.

Surface Tensiometry. Surface tension measurements were carried out using a Kruss K10ST surface tensiometer equipped with a platinum ring. Either the copolymer concentration of the selectively quaternized block copolymers or the solution pH were varied. The pH was monitored using a Corning Check-Mite pH sensor calibrated with pH 4, 7, and/or 10 buffer solutions.

Results and Discussion

Quaternization of Tertiary Amine Methacrylate Homopolymers. The quaternization of amines by alkyl halides is known as the Menschutkin reaction and was first reported over a hundred years ago.[24] Significant steric effects were noted in these original small-molecule studies, with tertiary amines reacting much more slowly than secondary or primary amines. Polymer-analogous reactions are also well-documented, particularly for the quaternization of DMA homopolymers[25−27] and various vinylpyridine homopolymers.[28−30] However, as far as we are aware, there have been no reports of the *selective*

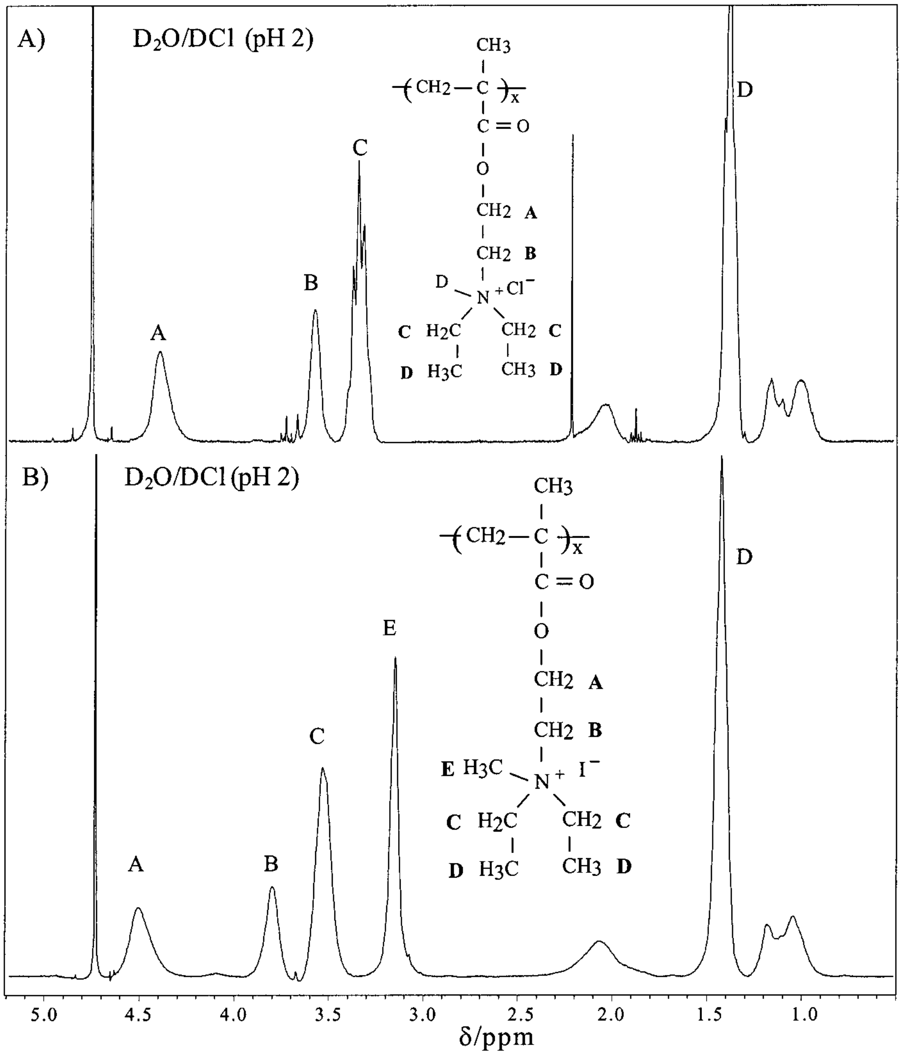

Figure 3. ^{1}H NMR spectra of DEA homopolymer: (a) before quaternization (D_2O/DCl) and (b) after quaternization with MeI (D_2O/DCl).

quaternization of copolymers containing two types of amine groups. In this paper we will demonstrate that DMA residues are significantly more reactive toward quaternization than DEA, MEMA, or DPA residues. This allows the *selective* quaternization of DMA-based diblock copolymers, which in turn leads to pronounced changes in both surface activity and also the propensity for these new cationic polymeric surfactants to undergo micellization.

Initially, some trial experiments were carried out using DMA, MEMA, DEA, and DPA homopolymers. Quaternization of these four homopolymers was examined in both THF and water using MeI and BzCl (see Figure 1). The results are summarized in Table 1. DMA and MEMA homopolymers both reacted readily with MeI at 20 °C in both THF and water. Methylation of DMA homopolymer was essentially complete within 10−20 min at 20 °C in either THF or water. MEMA homopolymer was fully methylated at 20 °C after 1−2 h (water) or 6−10 h (THF). Complete methylation of DEA homopolymer required 2−4 h in THF at 20 °C but DPA homopolymer required 4 days at 45 °C for complete methylation in this solvent (see Table 1). Homopolymers quaternized with MeI in THF were typically yellow but white polymers were obtained using MeI in aqueous media. Thus, water was preferred as a solvent for quaternization with MeI wherever possible, even though this reagent has limited solubility in aqueous solution and is normally prone to hydrolysis. Unfortunately, neither DEA nor DPA homopolymers are water-soluble at neutral pH so quaternization could not be attempted in aqueous solution (both homopolymers dissolve in acidic media but quaternization is extremely slow under these conditions because the tertiary amine groups are protonated and therefore unreactive). It is interesting to note here that DEA or DPA residues residing within block copolymer micelle cores can be successfully quaternized using MeI at 20 °C (see later). In this case the reaction rate may be enhanced by preferential partitioning of the poorly soluble MeI within the hydrophobic micelle interior. BzCl proved much less reactive toward quaternization than MeI, as expected. Only DMA homopolymer could be fully quaternized with BzCl and this required aggressive reaction conditions (48 h at reflux). Only 5−10% benzylation was achieved for DPA and MEMA homopolymers under the same conditions.

The extent of quaternization was assessed using ^{1}H NMR spectroscopy. For example, Figure 2a shows the ^{1}H NMR spectrum of the DMA homopolymer in D_2O with all the relevant signals assigned. Peak C at δ 2.3−2.4 represents the six dimethylamino protons. After quaternization of this homopolymer with MeI (see Figure 2b), nine quaternary ammonium protons appear at δ 3.3. Comparison of the peak integral of this signal

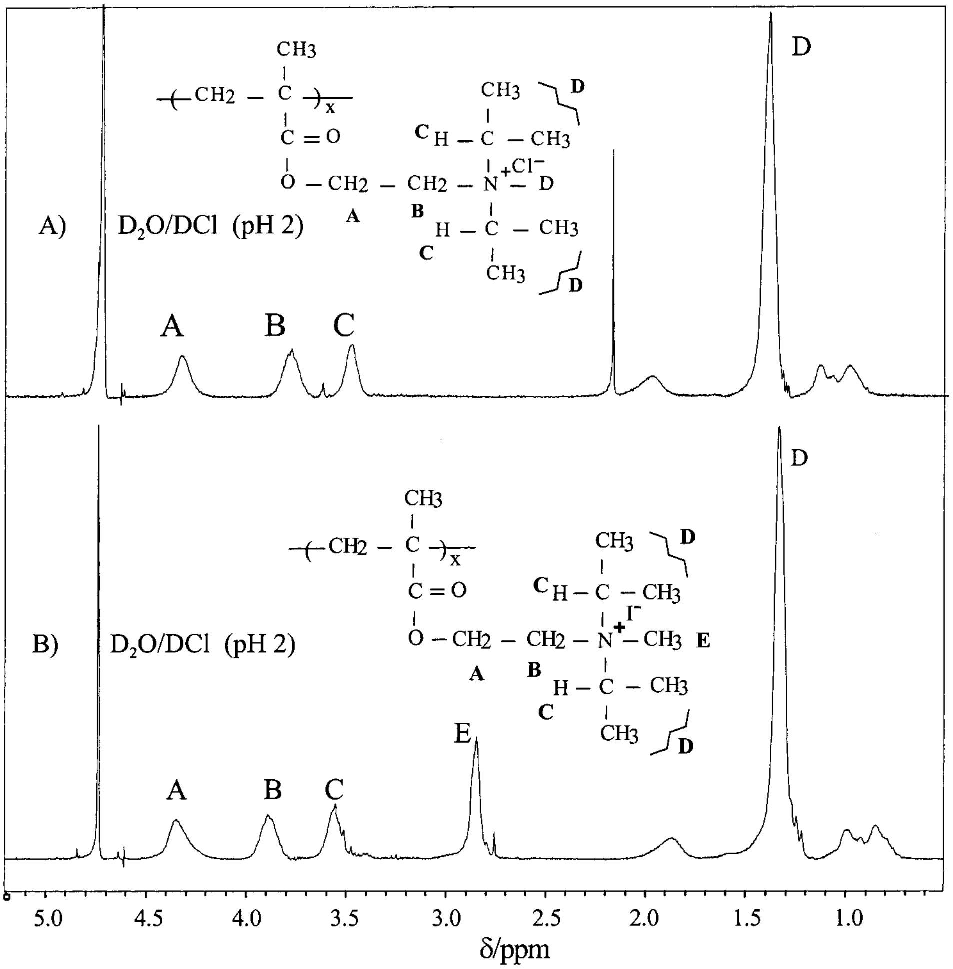

Figure 4. ^{1}H NMR spectra of DPA homopolymer in D_2O/DCl (pH 2): (a) before quaternization and (b) after quaternization with MeI.

with that of the oxymethylene proton signal at δ 4.1 indicates 100% quaternization. The absence of any unquaternized dimethylamino protons at δ 2.3−2.4 in Figure 2b confirms this calculation. In addition, Figure 2c shows the assigned NMR spectrum of the fully benzylated DMA homopolymer: in this case the degree of quaternization was determined by comparing the peak integral for the five aromatic protons at δ 7.5 with that of the six dimethylamino protons at δ 3.1.

After quaternization of the DEA homopolymer, peaks A, B, and C are shifted downfield from δ 3.3, 3.6, and 3.9 (see Figure 3a) to δ 3.5, 3.8, and 4.5 (see Figure 3b), respectively. A new peak, E, appeared at δ 3.1−3.2 because of the quaternary methyl group. The integrals of peaks E and A were compared and a degree of quaternization of ≈100% was determined. Several of the DPA signals are also shifted downfield from δ 3.4−3.5, 3.8, and 4.3−4.4 to δ 3.5−3.6, 3.9, and 4.3−4.4, respectively, after quaternization (see Figure 4a,b). A degree of quaternization of 65% after 2 days in refluxing THF was determined by comparing the peak integrals of the quaternary methyl proton signal at δ 2.8−2.9 to that of the four equivalent methyl groups at δ 1.4. After 6 days in refluxing THF the degree of quaternization was 100%. For the quaternized MEMA homopolymer, downfield shifts from δ 2.6, 2.8, 3.8. and 4.2 to δ 3.7, 4.1, 4.2. and 4.6 were observed (compare Figure 5a and 5b). The quaternary methyl protons are at δ 3.4 (see Figure 5b). Comparing the peak integrals of signals E and A suggested that quaternization was complete and the absence of any peak at δ 2.5−2.8 supported this conclusion.

For both MeI and BzCl, the relative ease of quaternization of the four tertiary amine methacrylate homopolymers is summarized in the following reactivity series: DMA ≫ DEA > MEMA ≫ DPA. These differences can be largely explained by the increasing steric crowding at the amine nitrogen. This steric congestion is probably comparable for the DEA and MEMA homopolymers, but the MEMA residues are significantly less basic, which probably accounts for their lower reactivity.[18,31]

Selective Quaternization of DMA Residues in DMA−DEA Diblock Copolymers. The homopolymer studies suggested that *selective* quaternization of the DMA residues in DMA−DEA, DMA−MEMA, or DMA−DPA diblock copolymers should be feasible, provided that suitably mild conditions and stoichiometric quantities of the alkylating reagent were employed. The results are summarized in Table 2. The NMR spectrum (recorded in D_2O/DCl at pH 2) in Figure 6a shows the assignment of all peaks corresponding to both blocks of a 49:51 DMA−DEA diblock copolymer. After benzylation, the signal I at δ 7.5 corresponds to the five aromatic protons of the benzyl groups and its integral was compared to that of signal C at δ 3.1−3.2 to determine a degree of quaternization of 100%; see Figure 6b.

In an earlier communication[17,18] we reported that DMA−DEA diblock copolymers exhibited highly pH-

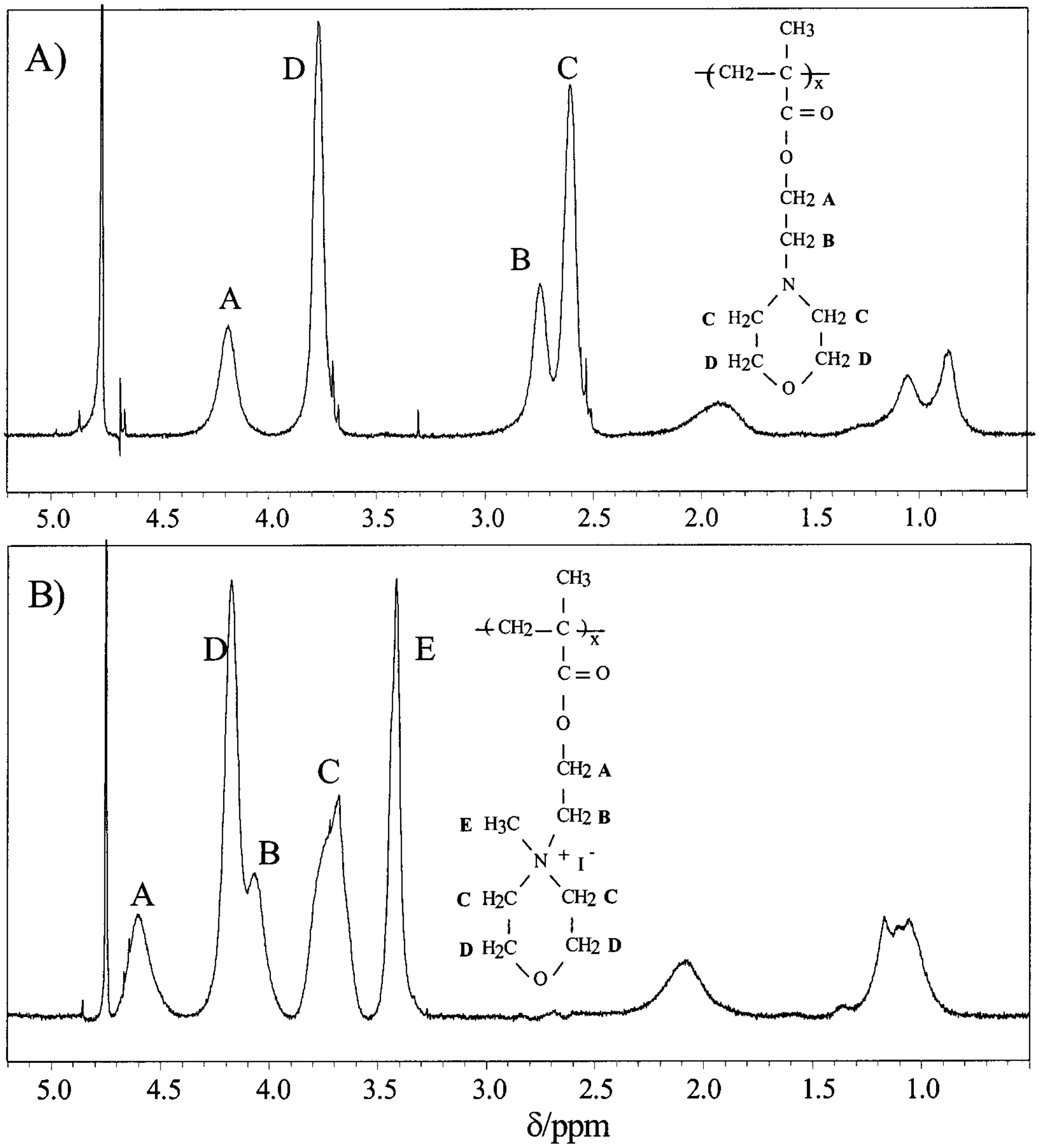

Figure 5. ^{1}H NMR spectra of MEMA homopolymer in D_2O: (a) before quaternization and (b) after quaternization with MeI.

Table 2. Summary of Block Copolymer Compositions, Molecular Weights, and Micelle Diameters of Selectively Quaternized DMA–DEA, DMA–DPA, and DMA–MEMA Diblock Copolymers (Quaternization Was Carried Out Using Either MeI or BzCl, Respectively; Micellization Conditions Were pH 12 and 20 °C)

sample code	selectively quaternized block copolymer	DMA content[a] (mol %)	precursor M_n[b] (g mol^{-1})	calcd. M_n[c] (g mol^{-1})	Na_2SO_4 concentration (M)	temp. (°C)	micelle diameter[d] (nm)
VB186	Me–DMA– DEA	34	35 000	44 600			23
VB153	Bz–DMA–DEA	50	15 000	20 550			15
VB155	Bz–DMA–DEA	49	9 550	13 000			10
VB154	Bz–DMA–DEA	78	12 400	19 900			
VB139	Me–DMA–DPA	82	11 550	19 550			14
VB138	Me–DMA–DPA	72	12 050	19 200			27
VB140	Me–DMA–DPA	61	15 750	23 200			33
VB223	Bz–DMA–DPA	82	11 550	18 700			15
VB156	Bz–DMA–DPA	72	11 800	18 000			30
VB136	Me–DMA–MEMA	46	25 500	34 750	0.1 M	20	unimers
VB136	Me–DMA–MEMA	46	25 500	34 750	0.1 M	65	25
VB136	Me–DMA–MEMA	46	25 500	34 750	1.0 M	20	27
VB132	Me–DMA–MEMA	35	36 000	45 700	0.1 M	20	unimers
VB132	Me–DMA–MEMA	35	36 000	45 700	0.1 M	65	34
VB132	Me–DMA–MEMA	35	36 000	45 700	0.8 M	20	39
VB220	Bz–DMA–MEMA	40	27 600	35 000	pH 10	20	unimers
VB220	Bz–DMA–MEMA	40	27 600	35 000	pH 10	65	35
VB220	Bz–DMA–MEMA	40	27 600	35 000	0.6 M	20	33

[a] As determined by ^{1}H NMR spectroscopy. [b] As determined by GPC [calibrated with poly(methyl methacrylate) standards]. [c] As calculated from GPC analyses of precursor polymers assuming 100% quaternization. [d] As determined by DLS on 1.0% aqueous solutions.

dependent surface activity and reversible micellization. It was suggested that the more hydrophobic DEA block adsorbed at the air–water interface and also formed the dehydrated micelle cores. Although the micelles formed by these polymeric surfactants are of interest, they are colloidally stable only over a relatively narrow pH range. Micellization occurs at around pH 7 and the micelles become unstable above pH 8–9 because of deprotonation

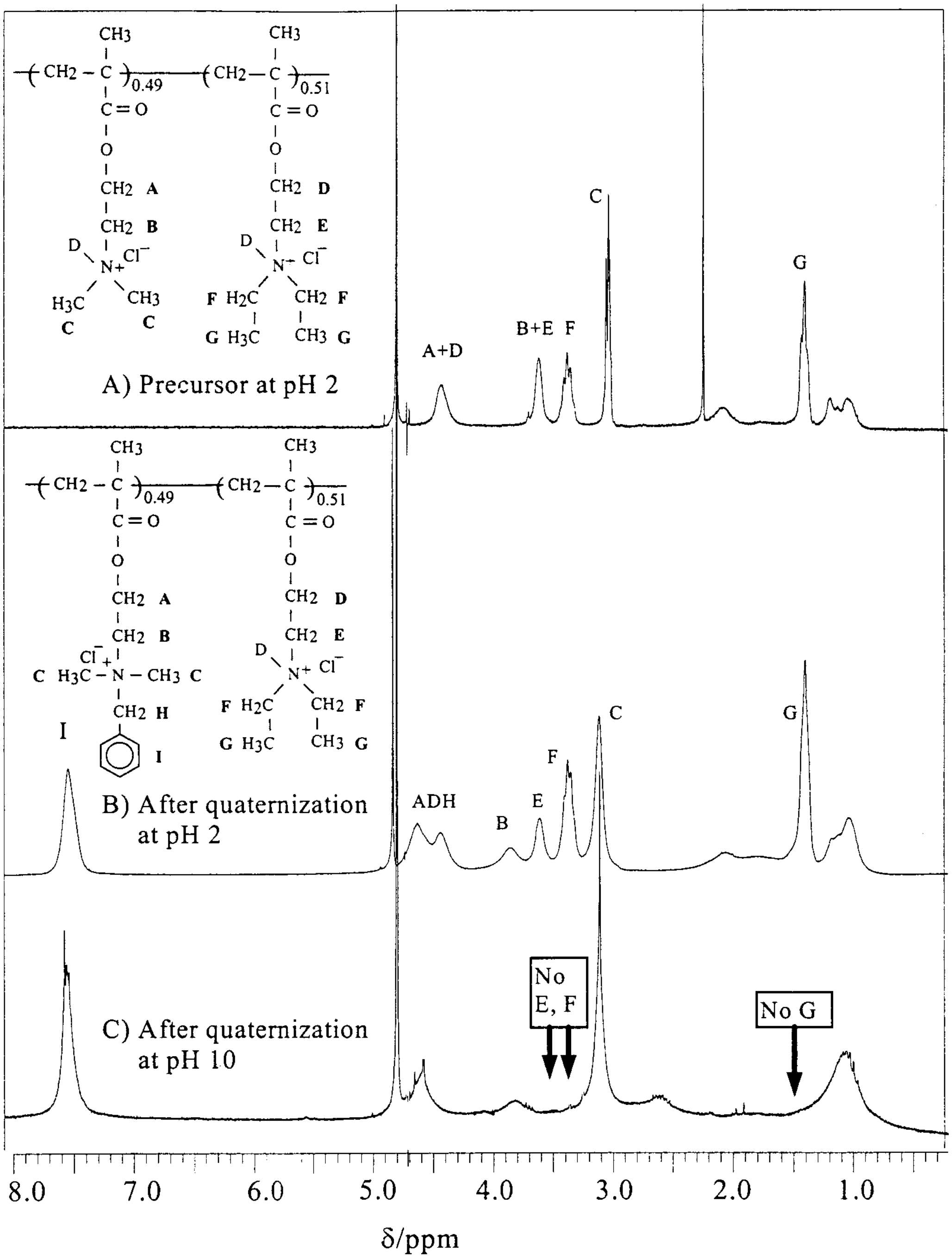

Figure 6. ^{1}H NMR spectra of a selectively benzylated 49:51 DMA–DEA block copolymer in D_2O: (a) precursor block copolymer at pH 2; (b) after quaternization at pH 2; (c) after quaternization at pH 12. Note the disappearance of the E, F, and G signals due to micellization of the unquaternized DEA block.

of the DMA blocks in the micelle corona (DMA homopolymer precipitates in alkaline media). However, selective quaternization of the DMA residues changes the aqueous solution behavior of these DMA–DEA diblock copolymers dramatically: micelles are stable over a much wider pH range (pH 7–12) because the quaternized DMA block is soluble in alkaline media. DLS studies (see Table 2) indicate micelle diameters of between 10 and 23 nm for the quaternized DMA–DEA diblocks, which are significantly lower than the micelles of 25–62 nm formed by the corresponding DMA–DEA precursor copolymers at the same pH. This is presumably because of the increased electrostatic repulsion between the cationic quaternary amine residues in adjacent copolymer chains within the micelle corona, which reduces the micelle aggregation number. Micelles with narrower polydispersities were observed at higher DEA block contents. NMR studies of the quaternized 49:51 DMA–DEA block copolymer confirm that the DEA block forms the micelle cores, as expected. As the solution pH is increased to pH 10, the peaks labeled E, F, and G corresponding to the DEA residues disappeared completely (see Figure 6c). This indicates that the DEA block becomes extensively dehydrated, while the signals due to the benzylated DMA block in the micelle corona remain visible at this pH.

Although selective quaternization of the DMA block does not prevent micellization, it significantly reduces the surface activities of these copolymers. For example, the surface tension vs pH profile of a selectively quaternized 78:22 DMA–DEA diblock indicates a limiting surface tension of only ≈55 mN m^{-1}, whereas the

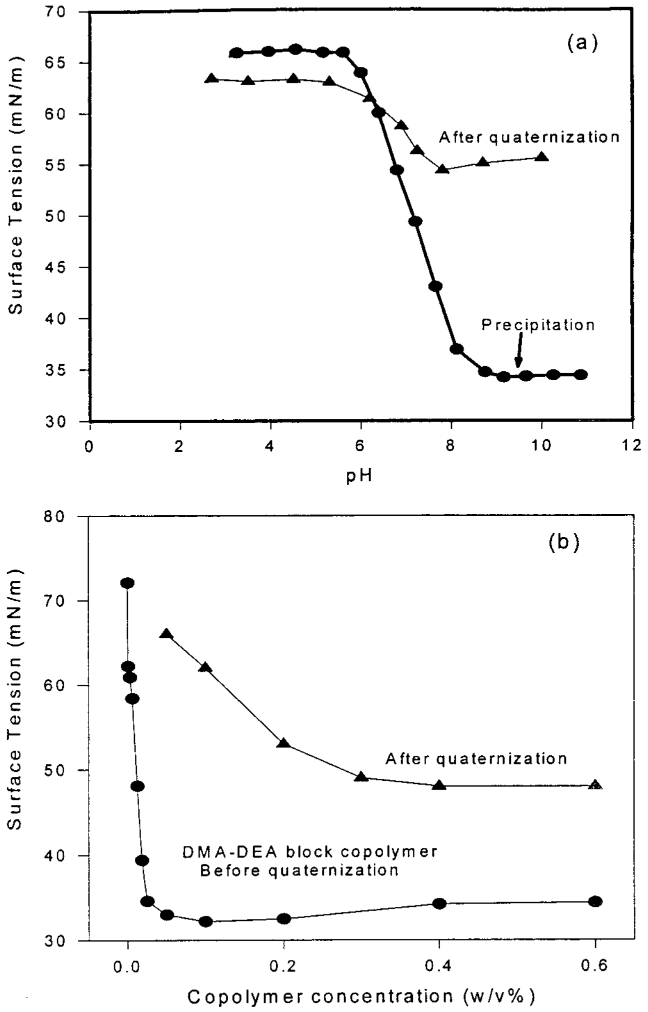

Figure 7. Variation of surface tension with (a) pH for a 0.2 w/v % aqueous solution of a 78:22 DMA–DEA diblock copolymer and (b) as a function of copolymer concentration at pH 8.5. Note that the selective quaternization of DMA residues (in this case with benzyl chloride) dramatically reduces the surface activity of these diblock copolymers.

precursor block is much more surface active, exhibiting a limiting surface tension as low as ≈34 mN m^{-1} (see Figure 7a). This is presumably due to the increased water solubility of the DMA block after quaternization, which reduces copolymer adsorption at the air–water interface. The CMC of the 78:22 DMA–DEA diblock is around 0.02 w/v % as estimated from the surface tension vs copolymer concentration curve (see Figure 7b). In contrast, the CMC of the selectively quaternized (in this case benzylated) DMA–DEA diblock is an order of magnitude higher at ≈0.3 w/v %. Similarly, the limiting surface tensions are 34 and 48 mN m^{-1} for the precursor and quaternized copolymer, respectively. Clearly, quaternization of these diblock copolymers decreases their surface activity significantly.

Selective Quaternization of DMA Residues in DMA-DPA Diblock Copolymers. Quaternization of DPA homopolymer with MeI is slow and requires long reaction times and high temperatures (see Table 1). Thus, selective quaternization of the DMA residues in a 61:39 DMA–DPA diblock copolymer was readily achieved both with MeI in THF at room temperature for 24 h and with BzCl in refluxing THF for 48 h. Figure 8a shows the NMR spectrum of the 61:39 DMA–DPA copolymer precursor in D_2O/DCl (pH 2). Under these conditions, both blocks are hydrophilic because the DPA residues are protonated. The peak integral of signal C at δ 3.2–3.3 due to the quaternary methyl protons was compared with that of signal G at δ 1.4 due to the unquaternized DPA residues to determine the block composition. The calculated block composition was the same as the precursor block composition, which indicates that all the DMA residues were quaternized. This conclusion is also consistent with the absence of any signal at δ 2.9–3.0 due to unquaternized dimethylamino protons. As the solution pH is increased to pH 9, the disappearance of the peaks due to the DPA residues at δ 1.3–1.4 indicated that the DPA block becomes dehydrated and forms micelle cores, with the quaternized DMA block forming the solvated micelle corona (see Figure 8c).

DLS studies confirmed that the micelle diameters of the quaternized DMA–DPA diblock copolymer were 14–33 nm, depending on the block composition (see Table 2). As the hydrophobic DPA content was increased, larger micelle diameters were obtained. Similar observations have been reported by Wooley and coworkers for partially quaternized 4-vinylpyridine–styrene diblocks.[32] Again, unlike the precursor copolymers, the selectively quaternized copolymers formed micelles that were stable at high pH, with no precipitation being observed, even at pH 12–13. However, in this case the differences in micelle diameter between the quaternized diblocks and the corresponding precursor copolymers are smaller compared to those observed for the DMA–DPA diblock copolymers.

Selective Quaternization of DMA Residues of DMA–MEMA Diblock Copolymers. The cloudpoint of MEMA homopolymer is slightly higher than that of DMA homopolymer.[18,31] Thus, DMA–MEMA diblock copolymers might be expected to exhibit temperature-induced micellization just above the cloudpoint of the DMA block, with the still-solvated MEMA chains forming the micelle coronas. However, in a preliminary study[33] Lowe found that well-defined micelles were not obtained; DMA–MEMA diblocks merely formed ill-defined, polydisperse aggregates prior to macroscopic phase separation. This was attributed to the relatively small difference (<5 °C) between the cloudpoints of the DMA and MEMA blocks. In principle, selective quaternization of the more reactive DMA residues with MeI or BzCl should produce much greater solubility differences between the two blocks; these derivatizations are summarized in Table 2.

Figure 9 shows the NMR spectra of a 46:54 DMA–MEMA diblock copolymer recorded in D_2O before and after quaternization of the DMA residues. The signal at δ 2.4 in Figure 9a is due to the six dimethyl amino protons of the DMA residues, whereas the complex signal at δ 2.5–2.8 corresponds to the six azamethylene protons in the MEMA residues. After selective quaternization with MeI, nine quaternary ammonium protons associated with the DMA residues appeared at δ 3.3 (see Figure 9b). Comparing this peak integral with that of the MEMA signal gives the same 46:54 copolymer composition as that determined for the original DMA–MEMA precursor block copolymer from Figure 9a. This confirms that the DMA residues were indeed selectively quaternized, as expected given the differing reactivities of the DMA and MEMA residues toward MeI observed in the homopolymer derivatization studies.

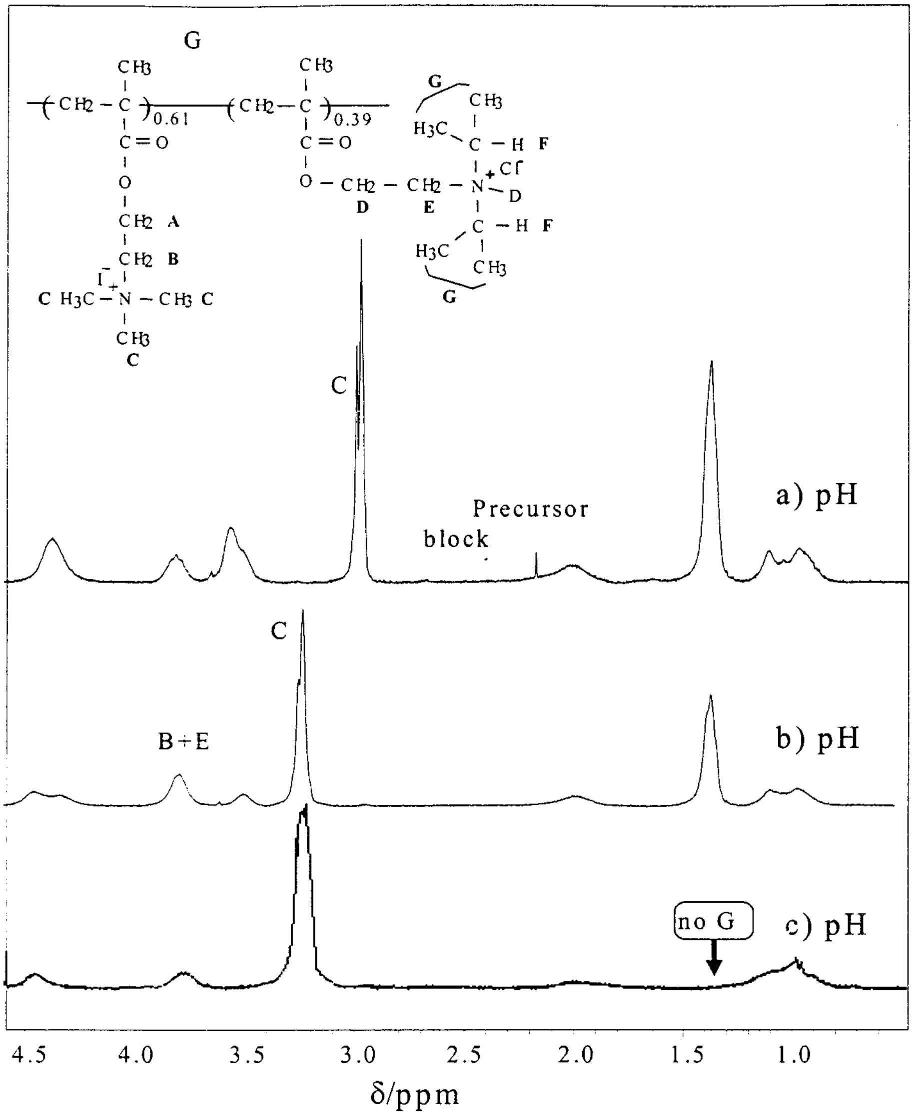

Figure 8. ^1H NMR spectra of (a) a 61:39 DMA−DPA precursor diblock copolymer in D_2O/DCl at pH 2 (VB140, M_n = 23 200 g mol^{-1}), (b) the same copolymer in D_2O/DCl at pH 2 after selective quaternization using MeI, and (c) the selectively quaternized copolymer at pH 9.

The quaternized DMA block is much more hydrophilic and no longer exhibits inverse temperature−solubility behavior at neutral pH. Thus, micellization is expected at temperatures above the cloudpoint of the MEMA block, with the MEMA block forming the micelle cores and the cationic DMA block forming the micelle coronas. This indeed proved to be the case. DLS measurements indicated micelle diameters of 25−35 nm at 65 °C (see Table 2) and NMR studies (not shown) confirmed that the MEMA signals broadened significantly at this temperature.

MEMA homopolymer is unusual in that it can be precipitated (salted out) from aqueous solution at 20 °C at relatively low salt concentration. Under the same conditions quaternized DMA homopolymer remains water-soluble (salting-out does occur eventually, but at much higher salt concentration). Thus, near-monodisperse micelles with polydispersities lower than 0.05 were obtained in the presence of either K_2CO_3 or Na_2SO_4, with the cationic DMA blocks forming the solvated coronas and MEMA blocks forming the micelle cores (see Table 2). ^1H NMR studies confirmed this intuitive interpretation because the MEMA signals disappeared in the presence of salt (compare Figure 9b,c), which is consistent with this block forming the dehydrated micelle cores. This micellization is reversible: as the salt is removed via dialysis, the MEMA block becomes solvated again.

In summary, selectively quaternized DMA−MEMA diblocks formed well-defined micelles both in the presence of low salt concentration (0.1 M) at 65 °C and in the presence of high salt concentration (1.0 M) at 20 °C. Micelle diameters ranged from 20 to 40 nm, depending on the block composition, overall chain length, and solution conditions.

Partial Quaternization of DMA-Based Diblock Copolymers. Partial quaternization of the DMA residues in the diblock copolymers was readily achieved using substoichiometric amounts of MeI. Under these conditions the DMA precursor block became a statistical copolymer containing both underivatized DMA and quaternized DMA residues. The degree of quaternization was determined from ^1H NMR spectra by comparing the corresponding peak integrals, as described earlier. Partially quaternized diblocks offer two advantages compared to fully quaternized diblocks: (1) their surface activities are much more similar to those of the corresponding precursor diblocks;[34] (2) further quater-

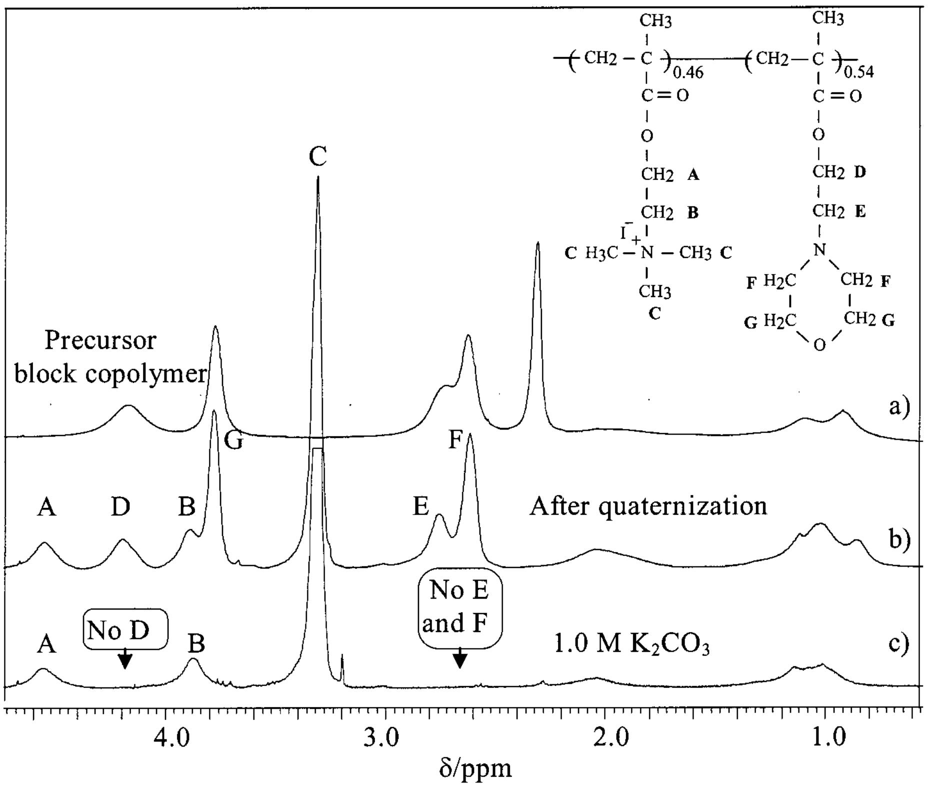

Figure 9. ^{1}H NMR spectra of a selectively quaternized 46:54 DMA–MEMA block copolymer in D_2O: (a) before selective quaternization; (b) after selective quaternization; (c) after selective quaternization and in the presence of 1 M K_2CO_3. Note the disappearance of the MEMA signals due to micellization in the latter case.

Table 3. Summary of Block Copolymer Compositions, Precursor Molecular Weights, and Calculated Molecular Weights of Selectively Betainized and Quaternized Block Copolymers

sample code	polymer	DMA content	precursor M_n[b]	calcd. M_n[c]	degree of quaternization[d]	solvent and pH
		(mol %)[a]	(g mol^{-1})	(g mol^{-1})	for second block	
VB134	BetDMA–MeDEA	51	32 600	57 400	100	water/pH 7–8[e]
VB146	BetDMA–MeDPA	72	12 050	25 300	100	water/pH 7–8[f]
VB145	BetDMA–MeMEMA	46	25 500	44 300	100	water/pH 7–8[e]

[a] As determined by ^{1}H NMR spectroscopy. [b] As determined by GPC [calibrated with poly(methyl methacrylate) standards]. [c] As calculated from GPC analyses of precursor polymers. [d] At 20 °C for 24 h. [e] At 20 °C for 24 h. [f] At 45 °C for 48 h.

nization of the remaining DMA residues using a bifunctional alkyl halide is a facile route to shell cross-linked micelles.[35–37]

Quaternization of Selectively Betainized Diblock Copolymers. The first examples of betainized–quaternized diblock copolymers were synthesized from DMA–MEMA, DMA–DEA, and DMA–DPA precursor copolymers (Table 3). First, selective betainization of the DMA residues in each diblock copolymer was achieved using 1,3-propane sultone in THF.[23] Quaternization of the MEMA, DEA, or DPA residues in the second block was then carried out using MeI in alkaline aqueous media (pH > 8). Under these conditions the MEMA block is soluble but the DEA and DPA blocks are hydrophobic and form micelle cores. Calculated molecular weights and reaction conditions are listed in Table 3.

Figure 10 shows the ^{1}H NMR spectrum of a betainized-DMA/quaternized-DEA copolymer, before and after quaternization of the DEA residues. Comparing the spectra in Figure 10a and 10b indicates that quaternization of DEA residues has occurred. Signal K corresponds to the methyl group bound to the nitrogen of the DEA residues after quaternization. In addition, several DEA signals, such as H and I, are shifted downfield to δ 3.5 and δ 3.7–3.8 after quaternization. Comparison of the peak integrals of the signals C and K indicated a degree of quaternization of ≈100%. Similar spectra were obtained with the betainized/quaternized DMA–DPA and DMA–MEMA diblock copolymers.

These betainized–quaternized blocks were expected to undergo salt-induced micellization, with the betainized (salt-liking) block forming the solvated micelle coronas and the quaternized (salt-hating) block forming the dehydrated micelle cores in each case. However, no micellization was observed, even at salt concentrations of up to 4 M KCl, as judged by DLS and ^{1}H NMR studies. Further studies on the aqueous solution behavior of these new copolymers will be carried out soon.

Conclusions

A series of tertiary amine methacrylate diblock copolymers based on DMA, MEMA, DEA, and DPA has been synthesized using GTP. Preliminary studies on the corresponding four homopolymers indicated that the DMA residues were much more reactive toward alkyl halides, which suggested that selective quaternization might be possible. This proved to be the case: the DMA residues in DMA–DEA, DMA–DPA, and DMA–MEMA

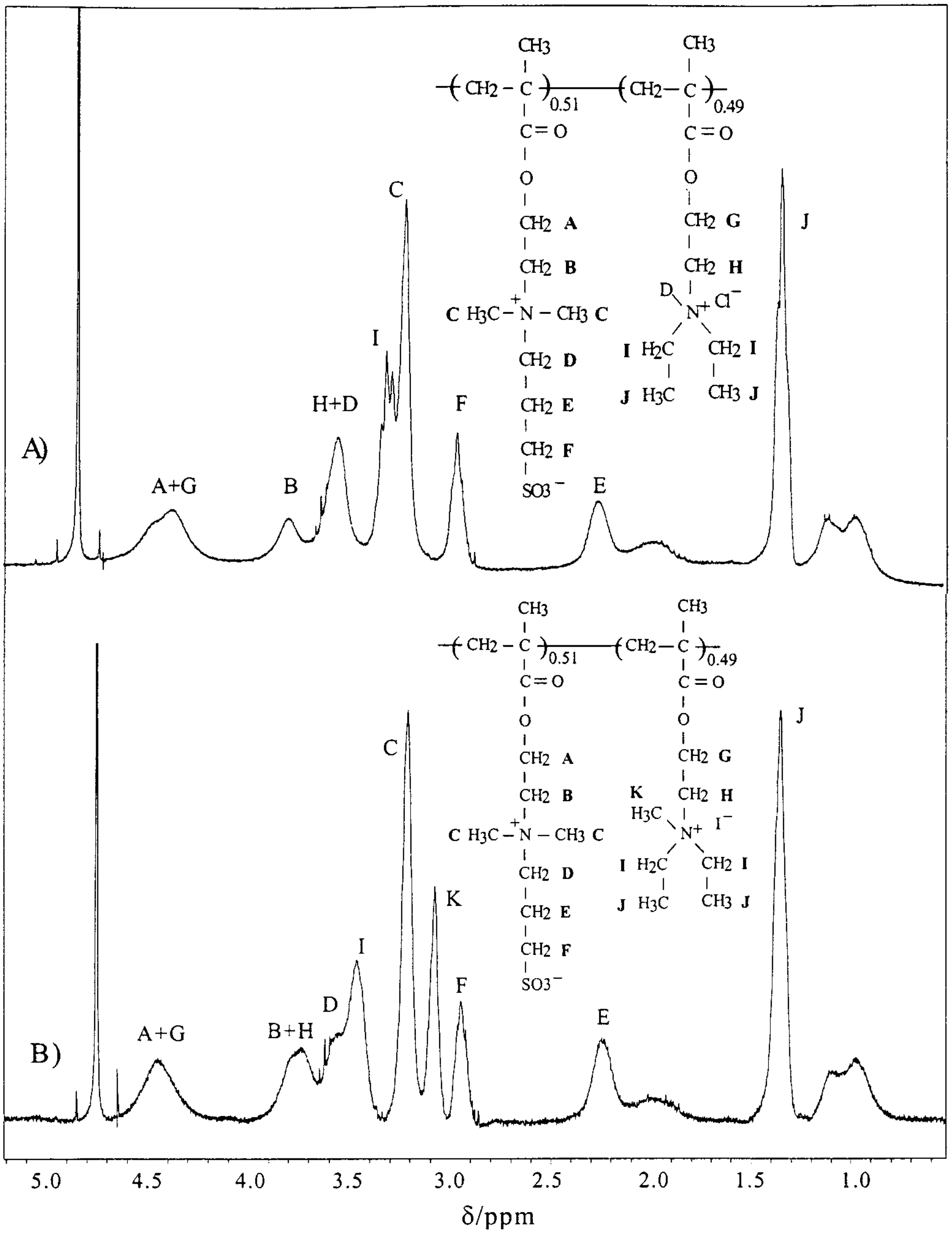

Figure 10. ^{1}H NMR spectra of (a) a selectively betainized DMA–DEA copolymer in D_2O (the DMA–DEA precursor copolymer contained 51 mol % DMA and had an M_n of 32 600 g mol^{-1}; VB134) and (b) after quaternization of the DEA block with MeI to produce a betainized DMA-quaternized DEA block copolymer.

diblock copolymers were successfully quaternized using both methyl iodide and benzyl chloride, producing a new range of cationic diblock copolymers.

Selective quaternization of the DMA residues produced much greater solubility differences between the block sequences. For example, unlike their precursor copolymers, selectively quaternized DMA–DEA and DMA–DPA diblocks both formed stable micelles at high pH. DLS studies indicated intensity-average micelle diameters of 14–40 nm and near-monodisperse micelles were obtained in some cases. However, quaternization significantly reduced the surface activities of these copolymers. Nevertheless, these new cationic diblocks exhibit interesting pH-regulated adsorption at the silica/water interface.[38] With the quaternized DMA–MEMA diblocks, the MEMA block became hydrophobic either at high temperature or in the presence of high salt concentration, leading to micelle formation.

^{1}H NMR studies confirmed that, for each type of diblock copolymer, the quaternized DMA residues formed the micelle coronas, with the micelle cores comprising MEMA, DEA, or DPA residues, respectively. Micellization was completely reversible in all cases. Finally, the first examples of betainized/quaternized diblock copolymers were also obtained from the same tertiary amine methacrylate precursor copolymers.

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References and Notes

(1) Hoogeveen, N. G.; Cohen-Stuart, M. A.; Fleer, G. J.; Frank, W.; Arnold, M. *Macromol. Chem. Phys.* **1996**, *197*, 2553–2564.
(2) Hoogeveen, N. G.; Cohen-Stuart, M. A.; Fleer, G. J. *Colloids Surf. A* **1996**, *117*, 77–88.

(3) Hoogeveen, N. G.; Cohen-Stuart, M. A.; Fleer, G. J. *J. Colloid Interface Sci*. **1996**, *182*, 133−145.
(4) Creutz, S.; Teyssie, P.; Jerome, R. *Macromolecules* **1997**, *30*, 6−9.
(5) Creutz, S.; van Stam, J.; Antoun, S.; De Schryver, F. C.; Jerome, R. *Macromolecules* **1997**, *30*, 4078−4083.
(6) Creutz, S.; van Stam, J.; De Schryver, F. C.; Jerome, R. *Macromolecules* **1998**, *31*, 681−689.
(7) Creutz, S.; Jerome, R.; Kaptijn, G. M. P.; van der Werf, A. W.; Akkerman, J. M. *J. Coatings Technol*. **1998**, *70*, 41−46.
(8) Zhang, X.; Xia, J. H.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5167−5169.
(9) Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 1763−1766.
(10) Baines, F. L.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1996**, *29*, 3416−3420.
(11) Baines, F. L.; Dionisio, S.; Armes, S. P.; Billingham, N. C. *Macromolecules* **1996**, *29*, 3096−3102.
(12) Baines, F. L.; Armes, S. P.; Billingham, N. C.; Tuzar, Z. *Macromolecules* **1996**, *29*, 8151−8159.
(13) An, S. W.; Thirtle, P. N.; Thomas, R. K.; Baines, F. L.; Billingham, N. C.; Armes, S. P.; Penfold, J. *Macromolecules* **1999**, *32*, 2731−2738.
(14) An, S. W.; Thomas, R. K.; Baines, F. L.; Billingham, N. C.; Armes, S. P.; Penfold, J. *J. Phys. Chem. B* **1998**, *102*, 5120−5126.
(15) An, S. W.; Thomas, R. K.; Baines, F. L.; Billingham, N. C.; Armes, S. P.; Penfold, J. *Macromolecules* **1998**, *31*, 7877−7885.
(16) An, S. W.; Thomas, R. K.; Baines, F. L.; Billingham, N. C.; Armes, S. P.; Penfold, J. *J. Phys. Chem. B* **1998**, *102*, 387−393.
(17) Bütün, V.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1997**, 671−672.
(18) Bütün, V.; Billingham, N. C.; Armes, S. P. submitted to *Polymer* **2001**, in press.
(19) Lee, A. S.; Gast, A. P.; Bütün, V.; Armes, S. P. *Macromolecules* **1999**, *32*, 4302−4310.
(20) Lowe, A. B.; Armes, S. P.; Billingham, N. C. *Chem. Commun.* **1997**, 1035−1036.
(21) Tuzar, T.; Pospisil, H.; Plestil, J.; Lowe, A. B.; Baines, F. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1997**, *30*, 2509−2512.
(22) Lowe, A. B.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1999**, *32*, 2141−2148.
(23) Bütün, V.; Bennett, C. E.; Vamvakaki, M.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Mater. Chem.* **1997**, *7*, 1693−1695.
(24) Menschutkin, N. *Ber. Dtsch. Chem. Ges.* **1895**, *28*, 1398−1407. (*J. Chem. Soc. Abstr*. **1895**, 385).
(25) Deboudt, K.; Delporte, M.; Loucheux, C. *Macromol. Chem. Phys*. **1995**, *196*, 303−314.
(26) Bogoeva-Gaceva, G.; Andonova, A. *Polymer* **1993**, *34* (18), 3934−3939.
(27) Pradny, M.; Lokaj, J.; Novatna, M.; Sevcik, S. *Makromol. Chem*. **1989**, *190*, 2229−2234.
(28) Brown, H. C.; Cahn, A. *J. Am. Chem. Soc.* **1955**, *77*, 1715−1723.
(29) Boucher, E. A. *Prog. Polym. Sci.* **1978**, *6* (2), 63−122.
(30) Arcus, C. L.; Hall, W. A. *J. Chem. Soc.* **1964**, *2*, 5995−5999.
(31) Bütün, V. Ph.D. Thesis, University of Sussex, Brighton, UK, 1999.
(32) Thurmond, K. B.; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1997**, *119*, 6656−6665.
(33) Lowe, A. B. Ph.D. Thesis, University of Sussex, Brighton, UK, 1997.
(34) Unali, F. Ph.D. Thesis, University of Sussex, Brighton, UK, 2000.
(35) Bütün, V.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1998**, *120*, 12135−12136.
(36) Bütün, V.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 4288−4289.
(37) Bütün, V.; Wang, X.-S.; de Paz Banez, M. V.; Robinson, K. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **2000**, *33* (1), 1−3.
(38) Styrkas, D. A.; Bütün, V.; Lu, J. R.; Keddie, J. L.; Armes, S. P. *Langmuir* **2000**, *16*, 5980−5986.

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