# Synthesis and Solution Properties of Water-Soluble Hydrophilic−Hydrophobic Block Copolymers

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ABSTRACT: A series of water-soluble diblock copolymers containing 2-(dimethylamino)ethyl methacrylate and various alkyl methacrylates has been synthesized using group transfer polymerization. These hydrophilic−hydrophobic copolymers have been characterized with respect to chemical composition and molecular weight by NMR spectroscopy, elemental microanalyses, and gel permeation chromatography. Block copolymers containing methyl methacrylate as the hydrophobic component were water-soluble provided that the hydrophilic monomer content was greater than 60 mol % of the overall block copolymer. Quaternization of the DMAEMA block with methyl iodide was near-quantitative and considerably enhanced the water-solubility of the copolymers. NMR studies, surface tension measurements, and photon correlation spectroscopy all indicated that the PDMAEMA-*b*-MMA block copolymers form micelles in deionized water. However, in acidic solution (pH 2), copolymer micellization occurred only in the presence of added electrolyte. The block copolymer micelles initially increased in size on addition of added electrolyte at pH 9.5. Further electrolyte addition led to macroscopic precipitation.

## Introduction

Since the pioneering work by Szwarc and co-workers,[1] controlled polymer architecture *via* "living" polymerization has been the subject of intensive world-wide research. It is well-known that sequential monomer addition allows the synthesis of block copolymers in which the comonomers can be selected to give the desired solid-state and solution properties. This has led to successful commercial products such as the Pluronic series of copolymer surfactants. Such block copolymers form micelles in solvents which are selective for one part of the block.[2,3] This phenomenon has been investigated for block copolymers in both aqueous and organic media.[3−5] Recently there has been increasing academic interest in hydrophilic−hydrophobic water-soluble (or water-dispersible) diblock copolymers. Since styrene is relatively straightforward to polymerize *via* classical anionic polymerization, many polystyrene-based block copolymers have been reported which incorporate a wide range of nonionic, anionic, and cationic hydrophilic components. For example, Barker and Vincent have synthesized poly(ethylene oxide-*b*-styrene) copolymers,[6] Munk and co-workers have synthesized and studied the micellization in aqueous solution of poly(styrene-*b*-methacrylic acid) copolymers,[7,8] and several groups have reported the synthesis and solution behavior of poly(styrene-*b*-vinylpyridine) copolymers.[9−15] Poly(alkyl methacrylates) have also been utilized as the hydrophobic component in conjunction with various hydrophilic comonomers such as poly(2-vinylpyridine)[16−18] and sulfonated poly(glycidyl methacrylate).[19] Usually the hydrophobic component confers considerable surface activity: many water-soluble block copolymers have been demonstrated to be effective stabilizers,[20,21] emulsifiers,[14,22] or dispersants.[23]

The "living" character of group transfer polymerization (GTP) also allows the synthesis of poly(meth)acrylate block copolymers of narrow molecular weight distribution *via* sequential monomer addition.[24] Prior to this work, hydrophobic poly(alkyl methacrylate) block copolymers containing a small percentage (up to 10% by mass) of hydrophilic poly(2-(dimethylamino)ethyl methacrylate) have been synthesized using GTP.[25] In this work, we describe the GTP synthesis of water-soluble block copolymers containing hydrophilic poly(2-(dimethylamino)ethyl methacrylate) as the major component and various alkyl methacrylates as the minor hydrophobic component.

## Experimental Section

**Materials.** All reagents were purchased from Aldrich, unless otherwise stated. Tetrahydrofuran (Fisons) was initially dried over sodium wire and then refluxed over potassium for 3 days prior to use. The dried solvent was stored over 4 Å molecular sieves and transferred into the reaction vessel *via* a double-tipped needle. The initiator, 1-methoxy-1-trimethylsiloxy-2-methyl-1-propene (MTS), was distilled and stored at −5 °C in a graduated Schlenk flask prior to use. All monomers were passed down a basic alumina column to remove the hydroquinone monomethyl ether inhibitor. Octyl methacrylate (Fluorochem) was stirred over calcium hydride, and then decanted and stirred with bis(dimethylamino)methylsilane (ABCR) prior to use. All other monomers were dried by stirring over calcium hydride for 24 h, stored at −20 °C, and were freshly distilled prior to use. Tetrabutylammonium bibenzoate catalyst (TBABB) was prepared by the method of Dicker *et al.*[26]

**Block Copolymer Syntheses.** All reactions were carried out under dry nitrogen. All glassware was heated overnight at 130 °C before use. Assembled glassware was then heated under vacuum to eliminate surface moisture. The preparation of a poly(2-(dimethylamino)ethyl methacrylate-*b*-methyl methacrylate) (PDMAEMA-*b*-MMA) copolymer typifies the general procedure for block copolymer syntheses: TBABB (10 mg, 2 mol % based on initiator) and MTS (0.20 mL) were added to THF (100 mL) at room temperature. The DMAEMA monomer (18.0 mL) was added dropwise at an approximate rate of 1 mL per minute *via* a canulla to this stirred solution. The reaction mixture was left stirring at room temperature until the reaction exotherm had abated (usually *ca.* 90 min). A homopolymer sample for GPC analysis was then extracted before the addition of the MMA comonomer (3.0 mL). Again, the reaction mixture was stirred for 1 h; then the polymerization was quenched by the addition of methanol (2 mL). The polymer was recovered by removing the solvent, using a rotary

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evaporator, before drying *in vacuo* for 2 days at room temperature. This procedure results in a copolymer containing 79 mol % DMAEMA and 21 mol % MMA by NMR spectroscopy, with an $M_n$ of *ca.* 21 000 g mol$^{-1}$ by GPC (see below). A shorthand notation is used to indicate the relative comonomer composition in the present study. Thus, in the above example, the copolymer is denoted 79:21 PDMAEMA-*b*-MMA. Polymers of differing comonomer compositions were produced by varying the amount of MMA added. Different copolymer molecular weights were obtained by varying the initiator concentration.

**Quaternization.** Quaternization was carried out at room temperature by reacting a 3-fold excess of methyl iodide with the copolymer in THF. The reaction was left stirring for 2 h, by which time the quaternized polymer had precipitated from solution. The polymer was purified by soxhlet extraction with THF (to remove excess methyl iodide and iodine) and dried in a vacuum oven overnight.

**Gel Permeation Chromatography.** Molecular weights and molecular weight distributions were determined using gel permeation chromatography (GPC). The GPC equipment consisted of a RI detector and either a combination of a Waters Styragel and a PLgel 5 $\mu$m mixed 'D' column or two of the latter columns in series. Calibration was carried out using PMMA standards (Polymer Laboratories), ranging from *ca.* 2000 to 53 000 g mol$^{-1}$. The eluent was THF (HPLC grade; stabilized with butylated hydroxytoluene) at a flow rate of 1 mL min$^{-1}$. Mark−Houwink parameters were not available for the copolymers; thus, all molecular weights are reported as PMMA equivalents.

**Nuclear Magnetic Resonance Spectroscopy.** All NMR spectra were recorded using a Bruker AC-P 250 MHz instrument using either $CDCl_3$ or $D_2O$ as solvents.

**Elemental Microanalysis.** CHN elemental microanalyses were carried out by MEDAC Ltd. at Brunel University, U.K.

**Thermogravimetric Analysis.** Thermogravimetric analysis (Perkin Elmer TGA-7 instrument) was utilized to estimate the water content of a PDMAEMA homopolymer. The sample was heated under a nitrogen atmosphere at a rate of 10 °C min$^{-1}$ from room temperature to 120 °C. A repeat heating cycle was carried out to check that the weight loss observed was indeed due to loss of water rather than degradation of the polymer.

**Surface Tension.** The surface tension ($\gamma$) measurements were carried out using a White Electrical Instrument Co. torsion balance and a platinum ring. All measurements were carried out at 20−21 °C. Solution temperatures were controlled by means of a thermostated water bath. Reproducibility was checked by frequent determination of the surface tension of deionized doubly-distilled water (72−73 mN m$^{-1}$).

## Results and Discussion

GTP was used to synthesize PDMAEMA homopolymers and block copolymers containing DMAEMA and MMA. Both the overall block copolymer chain length and the length of the PMMA hydrophobe were varied. In addition, a series of four block copolymers each containing 80 mol % DMAEMA and 20 mol % of either methyl, ethyl, *n*-butyl, or *n*-octyl methacrylate were synthesized.

The effect of the order of monomer addition on the preparation of block copolymers was studied. Originally we had envisaged polymerizing the MMA comonomer first. In principle, this would allow accurate molecular weight determination for the extracted homopolymer (using GPC calibrated with PMMA standards) prior to the addition of the DMAEMA comonomer. In practice, the GPC trace of the final block copolymer revealed the presence of a small amount (<5%) of PMMA homopolymer. Since a study of the aqueous solution properties of these polymers was planned, even a small amount of water-insoluble PMMA homopolymer was considered undesirable. To avoid such contamination, all subsequent block copolymers were synthesized by polymerizing DMAEMA first, followed by the alkyl methacrylate monomer. Since the PDMAEMA homopolymer is water-soluble, contamination of the block copolymers is unlikely to adversely affect their solution properties. On the other hand, the GPC data for the extracted PDMAEMA homopolymer samples are probably less reliable since only secondary (PMMA) standards were available for calibration.

**Table 1. Gel Permeation Chromatography Results for PDMAEMA-*b*-MMA Copolymers: Comparison of a "Combined Styragel/PLgel GPC Column" Setup with a "Two PLgel GPC Column" Setup**

| | | Styragel + PLgel column setup[a] | | two PLgel column setup[a] | |
|---|---|---|---|---|---|
| sample ID | theor $M_n$ (g mol$^{-1}$) | $M_n$ (g mol$^{-1}$) | $M_w/M_n$ | $M_n$ (g mol$^{-1}$) | $M_w/M_n$ |
| FB068 | 9 500 | 10 500 | 1.20 | 12 800 | 1.12 |
| FB052 | 9 900 | 9 400 | 1.18 | 11 100 | 1.13 |
| FB054 | 10 800 | 12 000 | 1.21 | 15 000 | 1.10 |

[a] THF eluent, refractive index detector, PMMA standards.

GPC analyses were carried out using two different column arrangements. Initially a Waters Styragel and a PLgel 5 $\mu$m mixed-bed 'D" column were used in series; in later experiments, two PLgel 5 $\mu$m mixed-bed 'D' columns were utilized. The GPC results for a selection of block copolymers obtained using these different sets of columns are listed in Table 1. The number-average molecular weights determined using the PLgel columns alone were invariably higher than those obtained using the combined Styragel/PLgel column system, and the polydispersities were somewhat lower. This is believed to be due to the adsorption of PDMAEMA onto the Styragel column, which would result in peak broadening and higher retention times (lower molecular weights). Polyamine adsorption on GPC columns has been observed by other workers and has been attributed to the presence of residual carboxylic functionalities on the surface of the column.[25] Thus, all subsequent (co)polymer GPC data reported in this study were obtained using the two PLgel columns in series so as to minimize these effects. The number-average molecular weights, polydispersity indices, and the theoretical molecular weights for each of the homopolymers and block copolymers are summarized in Tables 2 and 3. In general, good agreement was observed between the theoretical and GPC molecular weights. All (co)polymers have low polydispersities ($M_w/M_n$ < 1.20), which is typical for methacrylate (co)polymers synthesized by GTP. As stated earlier, each of the block copolymers described in this work was synthesized by polymerizing the DMAEMA monomer first, which constitutes the major component of all the block copolymers. Due to the relatively small differences between the molecular weights of the homopolymer and block copolymer, any homopolymer contamination that might be present cannot be resolved (see Figure 1). However, in a related project, we have recently shown that the cross-over initiation efficiency for MMA-rich DMAEMA-*b*-MMA block copolymers is greater than 96.5% when the DMAEMA comonomer is polymerized first.[27]

$^1$H NMR spectroscopy was used to obtain the relative comonomer composition of the block copolymers. The NMR signal at $\delta$ 2.2−2.3 due to the six dimethylamino protons of the DMAEMA comonomer was ratioed to the signal at $\delta$ 3.5−3.6 assigned to the three methoxy protons of the MMA comonomer. Good agreement was obtained between the measured copolymer compositions and the theoretical values (see Table 4). The error in

**Table 2. PDMAEMA-*b*-MMA Copolymers with Theoretical Number-Average Molecular Weights for the DMAEMA Homopolymers of 8 500 and 17 000 g mol$^{-1}$, Respectively**

| sample ID | theor DMAEMA content (mol %) | theor $M_n$ of DMAEMA homopolymer (g mol$^{-1}$) | $M_n$ of DMAEMA homopolymer by GPC$^{a,b}$ (g mol$^{-1}$) | theor $M_n$ of block copolymer (g mol$^{-1}$) | $M_n$ of block copolymer by GPC$^{a}$ (g mol$^{-1}$) | $M_w/M_n$ of PDMAEMA-PMMA block copolymer |
|---|---|---|---|---|---|---|
| FB079 | 100 | 8 500 | 10 300 | | | |
| FB068 | 83.5 | 8 500 | 11 200 | 9 500 | 12 800 | 1.12 |
| FB052 | 79 | 8 500 | 9 300 | 9 900 | 11 100 | 1.13 |
| FB054 | 70 | 8 500 | 10 700 | 10 800 | 15 000 | 1.10 |
| FB069 | 59 | 8 500 | 9 400 | 12 300 | 12 200 | 1.13 |
| FB084 | 100 | 17 000 | 17 900 | | | |
| FB035 | 83.5 | 17 000 | 20 600 | 19 000 | 23 800 | 1.10 |
| FB070 | 79 | 17 000 | 16 200 | 19 900 | 19 600 | 1.14 |
| FB055 | 70 | 17 000 | 21 100 | 21 700 | 24 300 | 1.10 |
| FB071 | 59 | 17 000 | 18 100 | 24 600 | 23 800 | 1.13 |

[a] PMMA calibration standards, RI detector, THF eluent. [b] Polydispersities ($M_w/M_n$) were 1.10−1.15 for all the DMAEMA homopolymers.

**Table 3. PDMAEMA-*b*-Alkyl Methacrylate Copolymers with a Theoretical Number-Average Molecular Weight for the DMAEMA Homopolymer of 17 000 g mol$^{-1}$**

| sample | alkyl meth-acrylate | obsd $M_n$ of homo-polymer$^{a}$ (g mol$^{-1}$) | theor $M_n$ of block copolymer (g mol$^{-1}$) | obsd $M_n$ of block copolymer$^{a}$ (g mol$^{-1}$) | $M_w/M_n$$^{a}$ |
|---|---|---|---|---|---|
| FB105 | methyl | 16 400 | 19 900 | 21 800 | 1.10 |
| FB117 | ethyl | 15 500 | 20 300 | 21 800 | 1.08 |
| FB104 | *n*-butyl | 15 100 | 21 100 | 22 600 | 1.11 |
| FB120 | *n*-octyl | 13 800 | 22 200 | 18 100 | 1.10 |

[a] As determined by GPC (reported as PMMA equivalents).

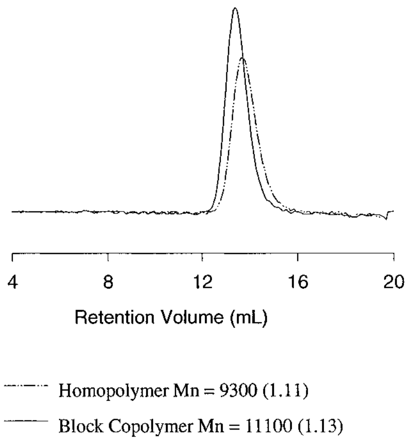

**Figure 1.** Typical gel permeation chromatograms of a PDMAEMA homopolymer and the corresponding PDMAEMA-*b*-MMA block copolymer (FB052).

**Table 4. Comparison of Block Copolymer Compositions As Determined Using $^1$H NMR Spectroscopy and CHN Elemental Microanalyses**

| sample | theor $M_n$ of block copolymer | theor DMAEMA content (mol %) | obsd DMAEMA content (mol %) | |
|---|---|---|---|---|
| | | | $^1$H NMR | microanalyses |
| FB068 | 9 500 | 83.5 ± 1.5 | 84 ± 2 | 82 ± 5 |
| FB052 | 9 900 | 79.0 ± 1.5 | 80 ± 2 | 77 ± 5 |
| FB054 | 10 800 | 70.0 ± 1.5 | 68 ± 2 | 63 ± 6 |
| FB035 | 19 000 | 83.5 ± 1.5 | 85 ± 2 | 80 ± 5 |
| FB070 | 19 900 | 79.0 ± 1.5 | 80 ± 2 | 73 ± 5 |
| FB055 | 21 700 | 70.0 ± 1.5 | 67 ± 2 | 70 ± 6 |

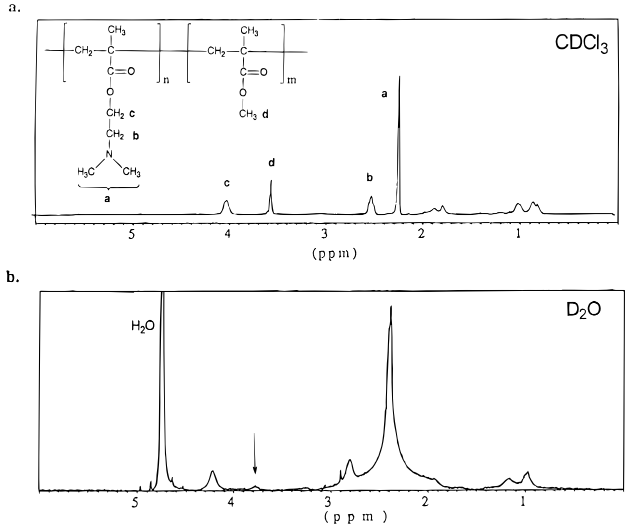

**Figure 2.** Typical $^1$H NMR spectra of a PDMAEMA-*b*-MMA block copolymer (FB054) in (a) a nonselective solvent ($CDCl_3$) and (b) a selective solvent ($D_2O$) for the hydrophobic PMMA component. Note the reduced intensity of the PMMA methoxy proton signal at $\delta$ 3.5−3.6 in the latter spectrum.

**Table 5. Effect of Block Copolymer Composition on the Water Solubility of PDMAEMA-*b*-Alkyl Methacrylate Copolymers**

| sample | alkyl methacrylate | obsd $M_n$ of block copolymer (g mol$^{-1}$)$^{a}$ | obsd DMAEMA content (mol %) | solubility in water |
|---|---|---|---|---|
| FB035 | methyl | 23800 | 85 | soluble |
| FB070 | methyl | 19600 | 80 | soluble |
| FB055 | methyl | 24300 | 67 | soluble |
| FB071 | methyl | 23800 | 59 | insoluble |
| FB117 | ethyl | 21800 | 83 | soluble |
| FB104 | n-butyl | 22600 | 81 | insoluble |
| FB120 | n-octyl | 18100 | 80 | insoluble |

[a] As determined by GPC (reported as PMMA equivalents).

compositions determined by this method was estimated to be approximately 2%. A typical $^1$H NMR spectrum for a PDMAEMA-*b*-MMA copolymer is shown in Figure 2a.

CHN elemental microanalyses were carried out on all the block copolymers in order to assess both comonomer composition and purity; comparisons were made with PDMAEMA homopolymers. The measured compositions agreed with theoretical values within experimental error (see Table 5). There are two possible sources of error in the measured values obtained by elemental analysis. First, the nitrogen content of the block copolymers and homopolymers is relatively low, at around 6.5 ± 0.3% and 8.0 ± 0.3%, respectively. Thus, we calculate an overall error of approximately ±6% in the calculated block copolymer composition values. Second, both the block copolymers and PDMAEMA homopolymers are relatively hydrophilic: thermogravimetric analysis of a PDMAEMA homopolymer sample revealed a small, variable water content of approxi-

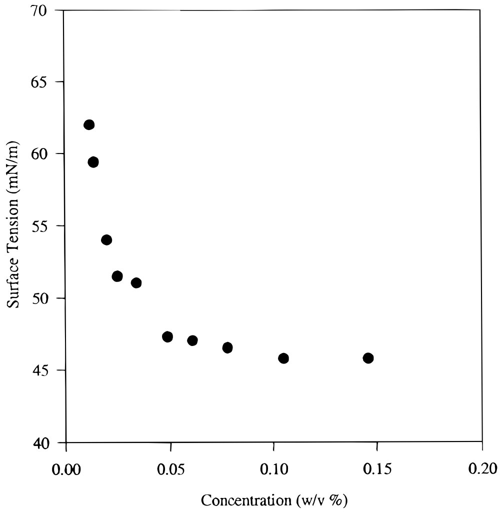

**Figure 3.** Variation of surface tension with block copolymer concentration for a PDMAEMA-*b*-MMA copolymer (FB052) in water at a solution pH of 9.5.

mately 2% by mass, which leads to slightly reduced carbon and nitrogen contents. For these reasons, the copolymer compositions determined by $^1$H NMR spectrocopy were considered to be more accurate than those calculated from CHN analyses.

The effects of copolymer composition and hydrophobicity of the alkyl methacrylate block on the water-solubility of the block copolymers are summarized in Table 5. The block copolymers containing DMAEMA and MMA can be fully dispersed in water when the DMAEMA content is greater than approximately 60–67 mol %. However, copolymers containing 80 mol % DMAEMA become water-insoluble as the alkyl methacrylate comonomer is made more hydrophobic, *e.g.* *n*-butyl or *n*-octyl methacrylate. However, it should be noted that all these block copolymers are readily soluble in dilute aqueous HCl. This is due to (at least partial) ionization of the amine groups in the DMAEMA component to produce a cationic polyelectrolyte. In general, water-soluble hydrophilic–hydrophobic block copolymers are expected to form micelles in water.[3–6] By analogy with low molecular weight surfactants, we expected to observe a critical micelle concentration (CMC) for the amphiphilic PDMAEMA-*b*-MMA block copolymers. The surface activity *vs* concentration profile for an 80:20 PDMAEMA-*b*-MMA copolymer in aqueous solution is shown in Figure 3. The surface tension decreases rapidly with increasing polymer concentration up to *ca.* 0.05 w/v %; above this concentration, the surface tension remains constant at around 46 mN m$^{-1}$. This behavior suggests that the critical micelle concentration (CMC) occurs at around 0.05 w/v %. This CMC value is very similar to that observed by Leemans *et al.*[19] for a hydrophilic–hydrophobic polyelectrolyte block copolymer of similar molecular weight comprising 76 mol % partially sulfonated glycidyl methacrylate and 24 mol % methyl methacrylate. A $^1$H NMR spectrum of a 68:32 PDMAEMA-*b*-MMA block copolymer in a nonselective solvent such as $CDCl_3$ is shown in Figure 2a. As expected, this spectrum confirms that both the DMAEMA and MMA components of the copolymer are well-solvated in this solvent (see, for example, the NMR signals at $\delta$ 2.2–2.3 due to the dimethylamino protons of the DMAEMA comonomer and $\delta$ 3.5–3.6 due to the methoxy protons of the MMA comonomer). On the other hand, in a selective solvent such as $D_2O$, the signal at $\delta$ 3.5–3.6 is suppressed since the hydrophobic PMMA component is only poorly solvated in this medium (see Figure 2b). Thus, above the CMC, both surface tension and $^1$H NMR data suggest that the block copolymers exist as micelles in aqueous solution: the core of the micelle contains the unsolvated PMMA component, with the PDMAEMA component acting as a solvated corona.

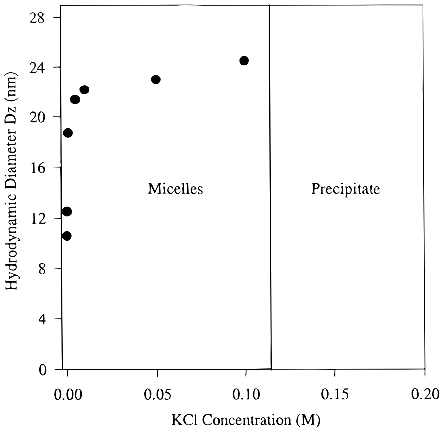

**Figure 4.** Effect of added salt (KCl) on the micellar dimensions of a PDMAEMA-*b*-MMA copolymer (FB052) dissolved in water at pH 9.5 as measured by photon correlation spectroscopy at 24 °C.

The quaternization of PDMAEMA has been reported by several workers.[28,29] In the present work, the PDMAEMA-*b*-MMA block copolymers were reacted with methyl iodide to form quaternized block copolymers. The degree of quaternization was found to be approximately 95–100 mol % using $^1$H NMR spectroscopy. Since quaternization of the amine groups in the PDMAEMA component yields a strong cationic polyelectrolyte, the derivatized block copolymers exhibited greatly enhanced solubility in aqueous solution compared to the unquaternized precursor blocks. As expected, these quaternized blocks were insoluble in most organic solvents (including relatively polar solvents such as methanol or THF) but were reasonably soluble in dipolar aprotic solvents such as DMSO. The surface activity of the quaternized copolymers was substantially reduced compared to the unquaternized materials.[27]

The effect of added salt on the aqueous solution behavior of the PDMAEMA-*b*-MMA copolymers was investigated by photon correlation spectroscopy (PCS). The very low light scattering intensity observed for these copolymers in acidic media (pH 2) suggests that the polymer chains are molecularly dissolved under these conditions.[30] However, micellization of a 79:21 PDMAEMA-*b*-MMA copolymer could be induced by addition of electrolyte (0.01–1.0 M KCl). This micelle diameter was determined to be *ca.* 27 nm by PCS. Similar observations of electrolyte-induced micellization have been reported by Selb and Gallot.[12] Upon dissolving the same copolymer in deionized water, the final solution pH was around 9.5, which suggests a small degree of ionization. PCS measurements indicated a micelle diameter of approximately 10.5 nm under these conditions (see Figure 4). When KCl is added to this micellar solution at pH 9.5, the hydrodynamic diameter of the micelles increases dramatically up to 24 nm over a relatively narrow salt concentration range (0–0.01 M). Above 0.01 M KCl, the block copolymer precipitates from solution. It is well-known that a cosolute can cause an increase or a decrease in the cloud-point of water-soluble polymers: hence, a water-soluble polymer may be precipitated (as in this case) or a water-insoluble polymer can be solubilized.[31] A more detailed description of micellization studies on these copolymers will be reported in the near future.[32] These block copolymers have also been evaluated as steric stabilizers for the dispersion polymerization of styrene in alcoholic media.[33]

## Conclusions

Group transfer polymerization has been used to synthesize water-soluble block copolymers containing hydrophilic poly(2-(dimethylamino)ethyl methacrylate) as the major component and various alkyl methacrylates as the minor hydrophobic component. These copolymers have been produced in quantitative yields. Good agreement was obtained between the calculated molecular weights and compositions of the copolymers and those determined using GPC and NMR spectroscopy, respectively. The effect of copolymer composition on water-solubility has been investigated. Copolymers which contained at least 67 mol % of the hydrophilic DMAEMA component were found to be water-soluble. All the copolymers are soluble in aqueous acid due to protonation of the tertiary amine groups in the DMAEMA component. The block copolymers can be precipitated from aqueous solution by addition of electrolytes such as KCl. Dynamic light scattering studies indicate micelle diameters of approximately 10−27 nm depending on the solution pH and electrolyte concentration. NMR studies suggest that the less-solvated MMA block was located in the micelle core, with the DMAEMA block comprising the micelle corona.

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(30) One of the reviewers has suggested that the very low light scattering intensity observed for the 'unimers' at pH 2 could be due to the "polyelectrolyte effect". Thus, the copolymer chains may be present as micelles (rather than unimers, as suggested in the text), and inter-chain repulsions may cause the micellar corona to be so diffuse that very little scattering is detected. In principle, static light scattering experiments as a function of added salt might allow us to distinguish between these two situations, but unfortunately our He−Ne laser-based light scattering instrument is not powerful enough to perform these experiments.
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