

**Annual Technical Progress Report**

**“Smart” Multifunctional Polymers for Enhanced Oil Recovery**

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by

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## Abstract

Herein we report the synthesis and solution characterization of a novel series of AB diblock copolymers with neutral, water-soluble A blocks comprised of *N,N*-dimethylacrylamide (DMA) and pH-responsive B blocks of *N,N*-dimethylvinylbenzylamine (DMVBA). To our knowledge, this represents the first example of an acrylamido-styrenic block copolymer prepared directly in homogeneous aqueous solution. The best blocking order (using polyDMA as a macro-CTA) was shown to yield well-defined block copolymers with minimal homopolymer impurity. Reversible aggregation of these block copolymers in aqueous media was studied by <sup>1</sup>H NMR spectroscopy and dynamic light scattering. Finally, an example of *core*-crosslinked micelles was demonstrated by the addition of a difunctional crosslinking agent to a micellar solution of the parent block copolymer. Our ability to form micelles directly in water that are responsive to pH represents an important milestone in developing “smart” multifunctional polymers that have potential for oil mobilization in Enhanced Oil Recovery Processes.

## EXECUTIVE SUMMARY

A coordinated, fundamental research program is underway in our laboratories with the *ultimate goal* of developing “*smart*” *multi-functional polymers* (SMFPs) that can respond *in situ* to stimuli (ionic strength, pH, temperature, and shear stress) resulting in *significantly improved sweep efficiency* in Enhanced Oil Recovery (EOR) processes. With these technologically “smart” polymers, it should be possible to produce more of the original oil in place and a larger portion of that by-passed or deemed “unrecoverable” by conventional chemical flooding. The *specific objectives* of this project are: a) to utilize *recent break-through discoveries* in the Polymer Science Laboratories at the University of Southern Mississippi to tailor polymers with the requisite structures and b) to evaluate the behavioral characteristics and performance of these multifunctional polymers under environmental conditions encountered in the petroleum reservoir. Two structural types of SMFPs are targeted that can work alone or in a concerted fashion in water-flooding processes. Type I SMFPs can reversibly form micelles, termed “polysoaps”, in water that serve to lower interfacial tension at the oil/water interface, resulting in emulsification of oil. Type 2 SMFPs are high molecular weight polymers designed to alter fluid viscosity during the recovery process.

Critical to the desired performance of these conceptual systems is the precise incorporation of selected functional monomers along the macromolecular backbone to serve as *sensors* or *triggers* activated by changes of the surrounding fluid environment. The placement of hydrophilic, hydrophobic, and triggerable monomers is accomplished by controlled free radical polymerization utilizing aqueous Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization, a technique under intensive development in the USM laboratories. The stimuli-responsive functional groups can elicit conformational changes in the polymers which in turn will alter surfactant behavior (type 1), viscosity (type 2), and permeability to the oil and aqueous phases. Thus, in principle, fluid flow behavior through the porous reservoir rock can be altered by changes in electrolyte concentration, pH, temperature, and flow rate. Significantly, the technology proposed is *environmentally attractive* since these systems can be synthesized in, processed in, separated from or recycled in *water*. Impetus for this study came from priority recommendations made during recent meetings organized by the Department of Energy and from extensive research over the past twenty-five years at USM on Water-Soluble Polymers. An infrastructure providing interdisciplinary research and academic studies in energy and environmental technologies, state-of-the art facilities and instrumentation, student stipends and scholarships, seminars and visiting scientists programs, and international symposia has been developed at USM almost exclusively from funding provided by the Chemical Flooding Program of the Department of Energy and the Environmental (Materials) Program of the Office of Naval Research. Over 70 students, including 40 PhDs have been trained in fossil energy and environmental technologies. Our current research has the added benefit of continuing the educational training of America’s future scientists and engineers and developing frontier EOR technologies critical to America’s economic security.

## Design and Synthesis of “Smart” Multi-Functional Polymers (SMFPs)

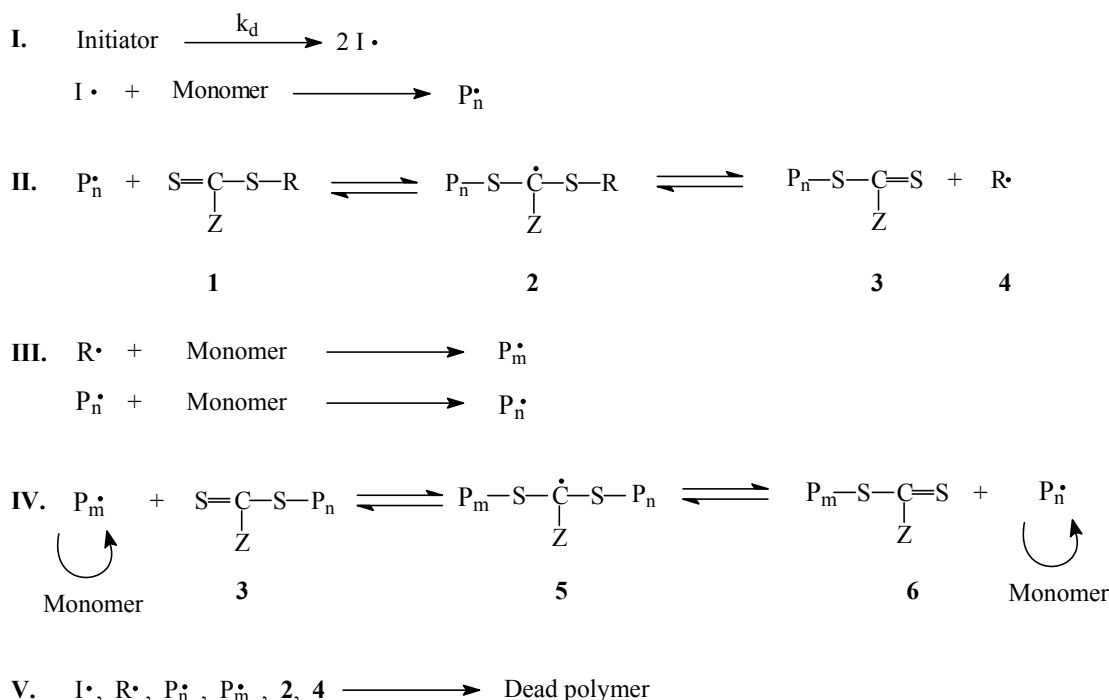
### INTRODUCTION

It is well known that amphiphilic block copolymers self-assemble to form multimolecular micelles in aqueous solutions.<sup>1,2</sup> Recent reports of such behavior in aqueous solution include the 2-(dimethylamino)ethyl methacrylate-methyl methacrylate block copolymers reported by Baines et al.,<sup>3,4</sup> the styrene-acrylic acid block copolymers reported by Zhang and Eisenberg,<sup>5</sup> and the 3-[*N*-(2-methacroyloxyethyl)-*N,N*-dimethylammonio]propane sulfonate-alkyl methacrylate block copolymers reported by Armes and coworkers.<sup>6,7</sup> The formation of well-defined micelles in aqueous media from inherently hydrophilic-hydrophobic block copolymers typically necessitates the use of an organic cosolvent. This cosolvent is non-selective and is normally employed to molecularly dissolve both blocks prior to the addition of water, which induces micellization. While these organic cosolvents can be readily removed by dialysis for example, it is clearly beneficial to prepare well-defined micelles in aqueous media without the need for organic cosolvents.

Recently, much effort has been focused on the synthesis of water-soluble copolymers that demonstrate responsive behavior when exposed to an external stimulus such as pH, temperature, or added electrolyte.<sup>8</sup> With the advancement of living polymerization techniques, there have been several reports of AB diblock copolymers that contain a hydrophilic block and another block that is tunably hydrophilic/hydrophobic or ‘smart’. This characteristic gives rise to stimuli-responsive surface activity such that well-defined micelles may be prepared without the need for organic cosolvents. The copolymer is simply molecularly dissolved in its hydrophilic-hydrophilic state, and micelle formation is induced by the gradual application of an appropriate stimulus, that renders the smart block hydrophobic.

While the traditional living polymerization techniques such as anionic, cationic, and group transfer polymerization provide a means of preparing well-defined block copolymers, these methods are limited by the requirements of stringent reaction conditions and/or low tolerance to functional groups. With the advent of controlled or ‘living’ free radical polymerizations,<sup>9</sup> it is now possible to prepare functional, block copolymers directly in aqueous media without the need for organic solvents or protecting group chemistry.<sup>10</sup> We have recently examined one such technique, namely reversible addition-fragmentation chain transfer (RAFT) polymerization.<sup>11</sup> The process, illustrated in Scheme 1, involves conventional free radical polymerization in the presence of a chain transfer agent (CTA) such as a dithioester. We utilized this process as a means for synthesizing neutral,<sup>12-14</sup> anionic,<sup>15-17</sup> cationic,<sup>15</sup> and zwitterionic<sup>10,18,19</sup> water-soluble (co)polymers, many of which have interesting aqueous solution properties. For instance, pH-responsive styrenic-styrenic<sup>15</sup> and acrylamido-acrylamido<sup>16,17</sup> block copolymers synthesized by aqueous RAFT were shown to undergo reversible self-assembly as a function of solution pH. Di- and triblock copolymers of *N,N*-dimethylacrylamide (DMA) and 3-[2-(*N*-methylacrylamido)-ethyldimethylammonio] propane sulfonate (MAEDAPS) were also prepared.<sup>19</sup> These block copolymers were molecularly dissolved in aqueous

salt solutions, since both blocks were solvated, but formed micelle-like aggregates in pure water due to dehydration of the MAEDAPS block under these conditions.



*Scheme 1.* Pathway for Reversible Addition-Fragmentation Chain Transfer polymerization.

Here we report the synthesis and solution characterization of a novel series of AB diblock copolymers with neutral, water-soluble A blocks (DMA) and pH-responsive B blocks (*N,N*-dimethylvinylbenzylamine (DMVBA)). To our knowledge, this represents the first example of an acrylamido-styrenic block copolymer prepared in homogeneous aqueous solution. The best blocking order was determined to yield well-defined block copolymers with minimal homopolymer impurity. Reversible aggregation of these block copolymers was studied by  $^1\text{H}$  NMR spectroscopy and dynamic light scattering. Finally, an example of core-crosslinked micelles was demonstrated by the addition of a difunctional crosslinking agent to a micellar solution of the parent block copolymer.

## EXPERIMENTAL

### Materials

All reagents were purchased from Aldrich at the highest purity available and used as received unless otherwise stated. 4,4'-Azobis(4-cyanopentanoic acid) (V-501) (**7**),

shown in Figure 1, was donated by Wako Chemicals and was recrystallized twice from methanol. Figure 2 shows *N,N*-dimethylacrylamide (**10**) and *N,N*-dimethylvinylbenzylamine (DMVBA) (**11**) which were vacuum-distilled prior to use. Figure 1 also shows 4-Cyanopentanoic acid dithiobenzoate<sup>15</sup> (**8**) and *N,N*-dimethyl-s-thiobenzoylthiopropionamide<sup>12</sup> (**9**) which were synthesized and purified as previously reported.

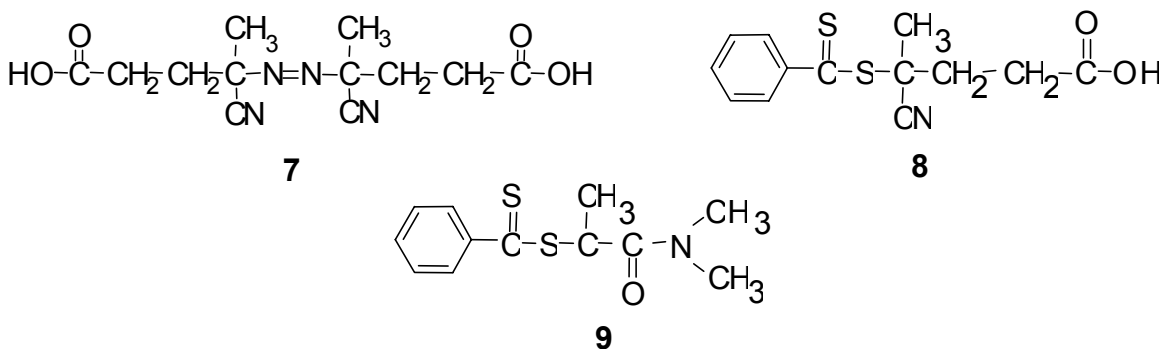


Figure 1. Initiator: 4,4'-azobis(4-cyanopentanoic acid) (V-501) (**7**) and chain transfer agents: 4-cyanopentanoic acid dithiobenzoate (CTP) (**8**) and *N,N*-dimethyl-s-thiobenzoylthiopropionamide (**9**).

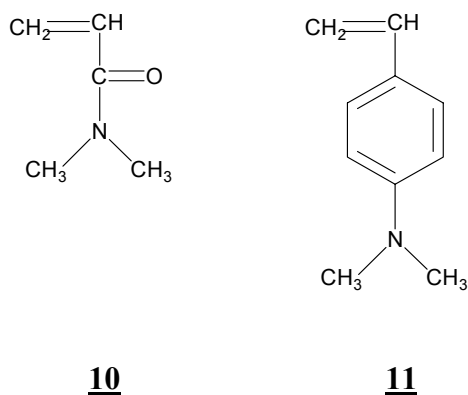


Figure 2. Structures of *N,N*-dimethylacrylamide (DMA) (**10**) and *N,N*-dimethylvinylbenzylamine (DMVBA) (**11**).

## Polymerizations

### *Synthesis of poly(N,N-dimethylvinylbenzylammonium chloride) (PDMVBAC)*



DMVBA (2.00 g, 12.4 mmol), 4-cyanopentanoic acid dithiobenzoate (CTP) (69.4 mg, 0.25 mmol), 4,4'-azobis(4-cyanopentanoic acid) (V-501) (16.3 mg, 0.058 mmol), and deionized water (13.0 mL) were added to a 50-mL round-bottomed flask equipped with a magnetic stir bar. Hydrochloric acid (6.0 M) was added to solubilize the monomer, and the solution pH was adjusted to 7.03. The flask was sealed with a rubber septum and the contents were purged with nitrogen for 30 min. The flask was immersed in a water bath preheated to 80 °C, and the polymerization was allowed to proceed for 24 h before being quenched by rapid cooling with liquid nitrogen. PDMVBA was isolated by precipitation into 2-propanol. The resulting polymer was dissolved in an equimolar amount of aqueous HCl and the solution was lyophilized to give poly(*N,N*-dimethylvinylbenzylammonium chloride) (PDMVBAC) (60 % yield).

*Synthesis of Poly(*N,N*-dimethylvinylbenzylamine-block-*N,N*-dimethylacrylamide) (P(DMVBA-*b*-DMA))*

PDMVBAC was employed as a macroCTA for the RAFT polymerization of DMA. PDMVBAC (1.01 g, 0.146 mmol), DMA (0.498 g, 5.02 mmol), V-501 (5.5 mg, 0.02 mmol), and deionized water (5.00 mL) were added to a 25-mL round-bottomed flask equipped with a magnetic stir bar. The solution was adjusted to pH 7.10, the flask was sealed with a rubber septum, and the solution was purged with nitrogen for 30 min. The flask was immersed in a water bath preheated to 80 °C, and the polymerization was allowed to proceed for 24 h before being quenched by rapid cooling with liquid nitrogen. The resulting polymerization solution was purified by dialysis against deionized H<sub>2</sub>O and the product was isolated by lyophilization (74 % yield).

*Synthesis of poly(*N,N*-dimethylacrylamide) (PDMA)*

*N,N*-dimethylacrylamide (12.0 g, 0.121 mol), *N,N*-dimethyl-*s*-thiobenzoylthiopropionamide (152 mg, 0.600 mmol), V-501 (18.4 mg, 0.0659 mmol), and deionized water (50.3 mL) were added to a 250-mL round-bottomed flask equipped with a magnetic stir bar and sealed with a rubber septum. The resulting solution was purged with nitrogen for 30 min, and the flask was immersed in a preheated water bath at 80 °C. The polymerization was allowed to proceed for 3.3 h before being quenched by rapid cooling with liquid nitrogen. The resulting polymerization solution was purified by dialysis against deionized water and lyophilized to give PDMA (24 % yield).

*Synthesis of Poly(*N,N*-dimethylacrylamide-block-*N,N*-dimethylvinylbenzyl-ammonium chloride) (P(DMA-*b*-DMVBAC))*

PDMA ( $M_n = 6600$  g/mol, PDI = 1.18) was employed as a macroCTA for three aqueous RAFT polymerizations of DMVBAC with V-501 as the free radical initiator. The appropriate amount of each reagent was added to glass vials equipped with magnetic stir bars (Table 1). 6.0 M HCl was added to solubilize the monomer, and the final solution pH was adjusted to  $7.15 \pm 0.05$ . The vials were sealed with rubber septa and the solutions were purged with nitrogen for 10 min. The polymerizations were allowed to proceed for 15.8 h at 70 °C before being quenched by rapid cooling with liquid nitrogen. The resulting polymerization solutions were purified by dialysis against deionized water and the block copolymers were isolated by lyophilization.

*Table 1.* Experimental Conditions Employed for the Synthesis of P(DMA-*b*-DMVBA) Block Copolymers.

	DMVBA		PDMA MacroCTA		V-501		H <sub>2</sub> O
	(g)	(mol x 10 <sup>3</sup> )	(g)	(mol x 10 <sup>5</sup> )	(mg)	(mol x 10 <sup>5</sup> )	(mL)
<b>P2</b>	0.573	3.56	0.418	6.33	4.3	1.51	4.50
<b>P3</b>	0.652	4.05	0.253	3.83	2.6	0.91	4.50
<b>P4</b>	0.430	2.67	0.181	2.74	1.8	0.66	4.50

## Instrumentation and Analysis

### *Micellar Solution Preparation*

Each block copolymer sample was dissolved in an equimolar (based on amine functionality) amount of HCl and the pH was adjusted to  $1.0 \pm 0.4$ . The resulting solutions were gently agitated for 36 h and subsequently filtered with 0.1  $\mu\text{m}$  Whatman Anotop syringe filters. Each solution was titrated with aqueous NaOH to yield 0.5 w/v % block copolymer solutions at pH  $10.0 \pm 0.3$ . After 7 days of gentle agitation, the resulting solutions were filtered (x 4) with 0.2  $\mu\text{m}$  Whatman Anotop syringe filters.

In order to prepare an example of core crosslinked micelles, a micellar solution of block copolymer **P2** was prepared as outlined above.  $\alpha,\alpha'$ -Dibromo-*p*-xylene (5 mol % with respect to amine units of DMVBA) was added at 6 °C, and the resulting solution was allowed to stir for 4 h at  $T < 10$  °C followed by 48 h at room temperature.

### *Aqueous Size Exclusion Chromatography (ASEC)*

ASEC was conducted with three Eichrom Technologies CATSEC columns calibrated with poly(2-vinylpyridine) (P2VP) standards. The mobile phase was 1 wt % acetic acid/0.1 M Na<sub>2</sub>SO<sub>4</sub> at a flow rate of 0.3 mL/min. The detectors included a Spectraphysics UV2000 UV-Vis detector and a Knauer K-2301 RI detector. Molecular weight and polydispersity data were calculated from software written in-house.

### *<sup>1</sup>H NMR Spectroscopy*

Samples were prepared as 0.5 w/v % solutions in D<sub>2</sub>O (HOD internal standard) with DCl or NaOD added for pH adjustment, and <sup>1</sup>H NMR spectra were recorded with a Bruker AC-300 spectrometer operating at 300 MHz.

### *Dynamic Light Scattering*

Dynamic light scattering (DLS) experiments were performed with 0.5 w/v % copolymer solutions using a Brookhaven Instruments 128-channel BI-2030 AT digital correlator equipped with a 25 mW Spectraphysics He-Ne laser operating at 632.8 nm.

Measurements were made at 90°, and CONTIN and CUMMULANTS analyses were used to fit the data.

## RESULTS AND DISCUSSION

### Block Copolymer Synthesis.

We recently demonstrated that the RAFT polymerizations of *N,N*-dimethylvinylbenzylammonium chloride (DMVBAC)<sup>15</sup> and DMA<sup>13</sup> in aqueous media proceed with excellent control over molecular weight and polydispersity. Employing these homopolymers as macro-chain transfer agents (macroCTAs) for subsequent copolymerizations facilitated the preparation of styrenic-styrenic<sup>15</sup> and acrylamido-acrylamido<sup>19</sup> block copolymers, respectively. While styrenic-acrylamido block copolymers have been prepared in organic media by various CRP techniques,<sup>20,21</sup> including RAFT,<sup>22-26</sup> to date there have been no examples of the block copolymerization of dissimilar monomer classes in water.

In this study, a homopolymer of DMVBAC was prepared in water with 4-cyanopentanoic acid dithiobenzoate and V-501 as the initiator and CTA, respectively. The PDI of the resulting DMVBAC homopolymer was 1.12, and the experimentally determined  $M_n$  of 5900 g/mol ( $DP = 30$ ) was in good agreement with the theoretical value of 6700 g/mol ( $DP = 34$ ). After purification and isolation, this homopolymer was employed as a macroCTA for the subsequent RAFT block copolymerization of DMA (Scheme 2A). Figure 3a shows the ASEC chromatograms for the DMVBAC homopolymer and DMVBAC-DMA block copolymer. While block copolymer formation is observed, there is also clearly residual homopolymer and significant high molecular weight impurity. Generally, residual homopolymer indicates that a portion of the macroCTA was not reactivated during the block copolymerization. This would be expected since the ASEC chromatogram for the PDMVBAC homopolymer indicates the presence of a significant amount of high molecular weight impurity, which is generally indicative of bimolecular termination. Terminated chains do not contain dithioester endgroups and are therefore incapable of reactivation and further monomer addition. The chromatograms also clearly show the presence of a high molecular weight impurity in the block copolymer. Thus the block copolymer is clearly not a well-defined species since it contains low and high molecular weight homopolymer impurities. The desired AB diblock copolymer and what is most likely other termination products formed during block copolymerization. When a similar water-soluble, styrenic-based homopolymer (poly(*ar*-vinylbenzyltrimethylammonium chloride) (PVBTA)) was employed as a macroCTA for DMA under the same conditions, even less well-defined block copolymers were obtained (Figure 3b).

Table 2. Results from the Aqueous RAFT Block Copolymerizations of DMA and DMVBA.

	Conv <sup>a</sup> (%)	$M_n$ Theory <sup>b</sup> (g/mol)	$M_n$ ASEC <sup>c</sup> (g/mol)	PDI ASEC <sup>c</sup>	$M_n$ NMR/ MALLS <sup>d</sup> (g/mol)	DP DMA	DP DMVBA	Composition (DMA/DMVBA) <sup>e</sup>
<b>PDMVBA MacroCTA</b>	60	5 900	6 700	1.12	-	-	34 <sup>c</sup>	-
<b>P(DMVBA<sub>34</sub>-<i>b</i>-DMA<sub>46</sub>)</b>	74	9 500	11 300	1.12	-	46 <sup>c</sup>	34 <sup>c</sup>	-
<b>PDMA MacroCTA (P1)</b>	24	4 800	4 900	1.17	6 600	67 <sup>d</sup>	-	100 / 0
<b>P(DMA<sub>67</sub>-<i>b</i>-DMVBA<sub>34</sub>)</b>	61	10 800	12 100	1.20	13 270	67 <sup>d</sup>	34 <sup>d</sup>	67 / 33
<b>P(DMA<sub>67</sub>-<i>b</i>-DMVBA<sub>50</sub>)</b>	51	14 000	14 300	1.17	16 370	67 <sup>d</sup>	50 <sup>d</sup>	58 / 42
<b>P(DMA<sub>67</sub>-<i>b</i>-DMVBA<sub>74</sub>)</b>	70	18 100	14 900	1.17	21 150	67 <sup>d</sup>	74 <sup>d</sup>	48 / 52

<sup>a</sup> Determined from the residual monomer concentration obtained from the RI detector during ASEC.

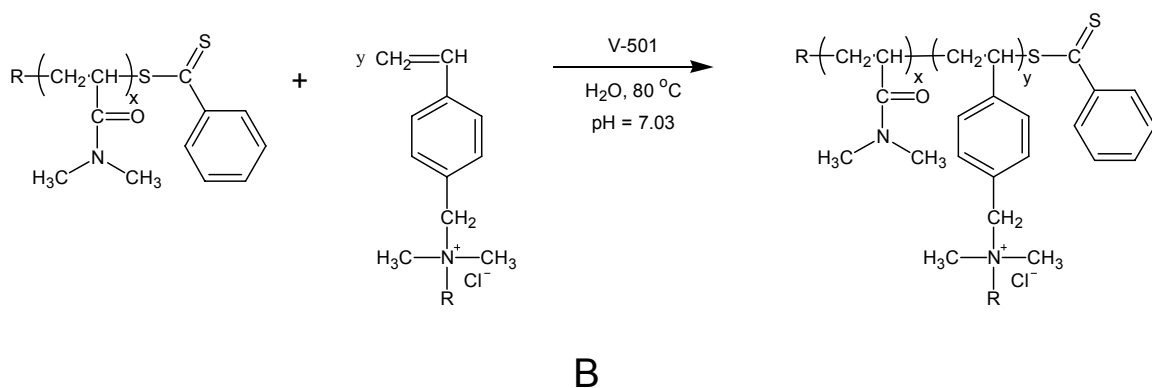
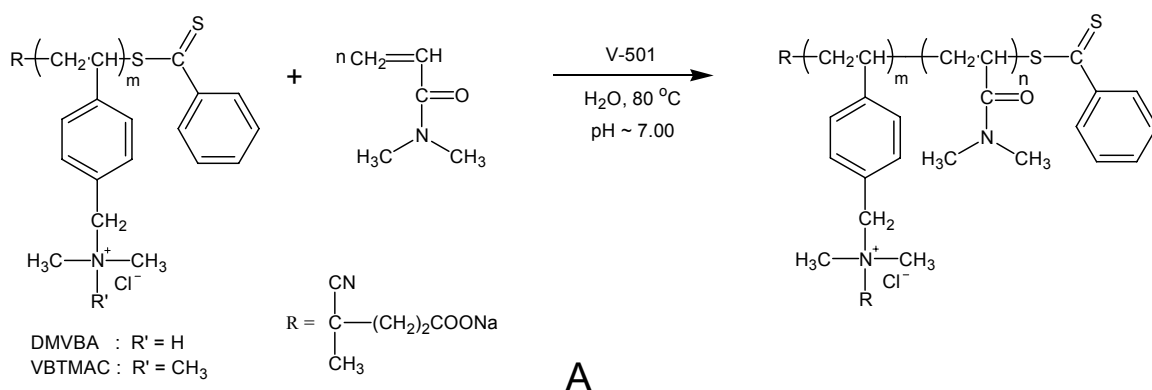
<sup>b</sup> Determined using  $M_n(\text{theory}) = [\text{Monomer}] \times [MW_{\text{mon}}] \times \text{conversion} / [\text{CTA}] + MW_{\text{macroCTA}}$ .

<sup>c</sup> Determined by ASEC with three columns calibrated with poly(2-vinylpyridine) (P2VP) standards.

Mobile phase: 1 wt% acetic acid/0.1 M Na<sub>2</sub>SO<sub>4</sub>, flow rate = 0.3 mL/min. Detectors included a UV-Vis and RI detector.

<sup>d</sup> Calculated by combining (1) the copolymer composition determined by <sup>1</sup>H NMR spectroscopy conducted in D<sub>2</sub>O/DCI and (2) the molecular weight of the PDMA macroCTA determined by MALLS.

<sup>e</sup> Determined by <sup>1</sup>H NMR spectroscopy conducted in D<sub>2</sub>O/DCI.



**Scheme 2.** Synthesis of a diblock copolymer of DMA and DMVBAC or VBTAC employing (A) a DMVBAC or VBTAC macroCTA and (B) a PDMA macroCTA.

It is well-known that when synthesizing AB diblock copolymers by sequential monomer addition, especially for blocks comprised of monomers from two different families, that the order of polymerization can be extremely important.<sup>11,22</sup> Therefore, the opposite blocking order was attempted in which a PDMA homopolymer **P1** ( $M_n = 6600$ , PDI = 1.18) was prepared by aqueous RAFT and subsequently employed as a macroCTA for the preparation of three block copolymers with different DMA/DMVBAC ratios (designated **P2-P4** in Table 1). Under these conditions, high blocking efficiency was observed with the resulting AB diblock copolymers having unimodal and narrow molecular weight distributions (Figure 4). This indicates all of the PDMA chains were functionalized with dithioester groups and were quantitatively reactivated. Additionally, the block copolymer traces show no signs of termination products, which could potentially lead to ABA triblock copolymers. These results are especially interesting, since, in organic media, well-defined styrene-DMA block copolymers have been reported utilizing polystyrene macroCTAs.<sup>22,23</sup> Our results indicate that, in water, DMA should be polymerized first when preparing block copolymers of DMA and DMVBAC or VBTAC.

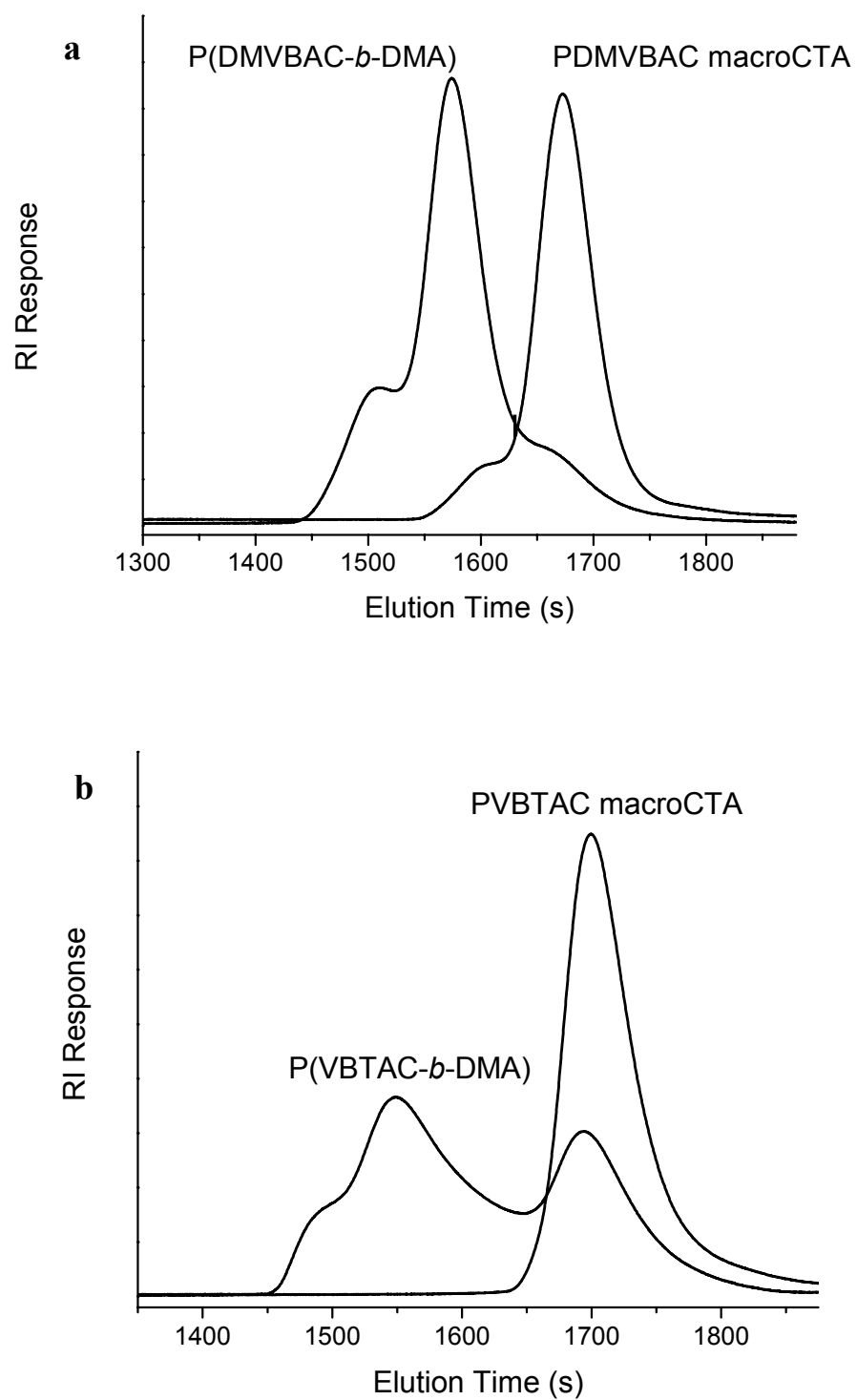


Figure 3. ASEC chromatograms for block copolymerization of DMA mediated with (a) a PDMVBAC macroCTA and a (b) PVBTAC macroCTA.

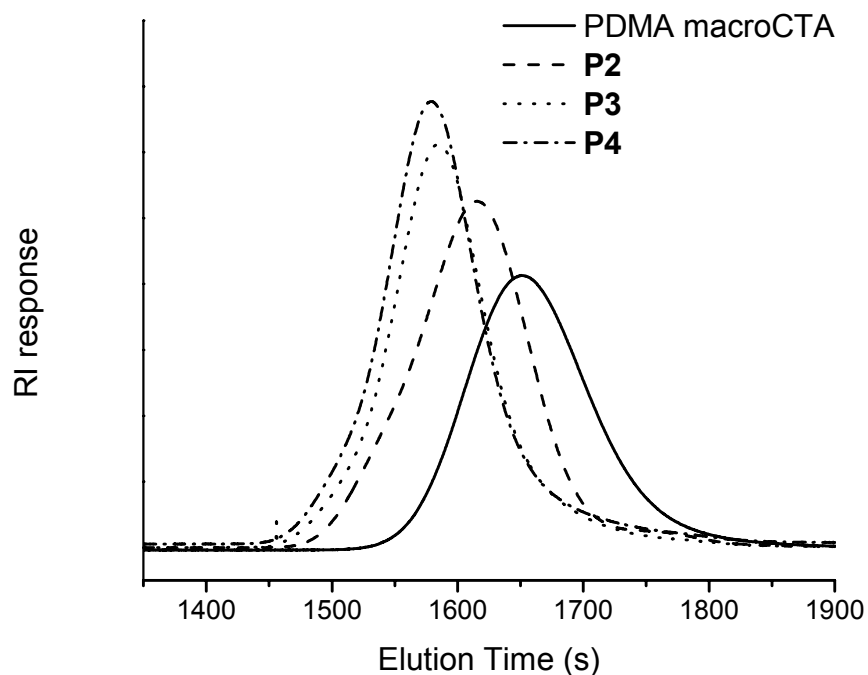


Figure 4. ASEC chromatograms for the PDMA macroCTA and three block copolymers with DMVBAC (**P2-4**).

These findings can be understood within the context of the RAFT mechanism by considering the factors that must be addressed when deciding the order of block copolymerization.<sup>27</sup> The chain end derived from the first monomer ( $A_n^\bullet$ ) must be capable of initiating polymerization of the second monomer (B), and the “leaving group ability” of  $A_n^\bullet$  must be greater than or comparable to that of  $B_m^\bullet$  under the specific polymerization conditions.

The low blocking efficiency observed when preparing the DMVBAC block first may be due to preferential fragmentation of the intermediate radical formed during the pre-equilibrium of the copolymerization to yield predominantly the DMA propagating chain. Alternatively, slow initiation of DMA by the PDMVBAC macroradical produced during fragmentation could lead to a similar result.

#### *Block Copolymer Composition and Molecular Weight Determination*

The  $^1\text{H}$  NMR spectra and peak assignments for block copolymer **P4** in  $\text{D}_2\text{O}/\text{DCl}$  at pH 1 is shown in Figure 5a. The acidic conditions were employed to ensure that all of the DMVBAC units were protonated. Integration of the methylene (*a*, *d*) and aromatic (*Ar*) peaks (Figure 5a) allows the calculation of compositions for **P2-4** according to Equation 1. These are tabulated in Table 2.

$$f_{DMA} = \frac{(A_{a,d} - A_{Ar} / 2) / 2}{A_{Ar} / 4 + (A_{a,d} - A_{Ar} / 2) / 2} \quad (1)$$

The molecular weights determined by ASEC are relative to 2VP standards (Table 2). While these standards may offer reasonable estimates of the molecular weight for DMVBAC homopolymers, they are inevitably poor for PDMA. Therefore, the number average molecular weight ( $M_n$ ) of the PDMA macroCTA was determined independently by ASEC coupled with a multi-angle laser light scattering (MALLS) detector. The value of  $M_n$  for the PDMA macroCTA determined by this method was 6900 g/mol as compared to 4900 g/mol obtained from ASEC. Using the molecular weight for the DMA homopolymer obtained by MALLS, coupled with the copolymer compositions determined by  $^1\text{H}$  NMR spectroscopy, the  $M_n$  values for the block copolymers were determined. Even with the error associated with  $^1\text{H}$  NMR spectroscopy ( $\pm 5\text{-}10\%$ ), these molecular weights may be more representative of the actual values since they do not rely on comparisons with primary standards.

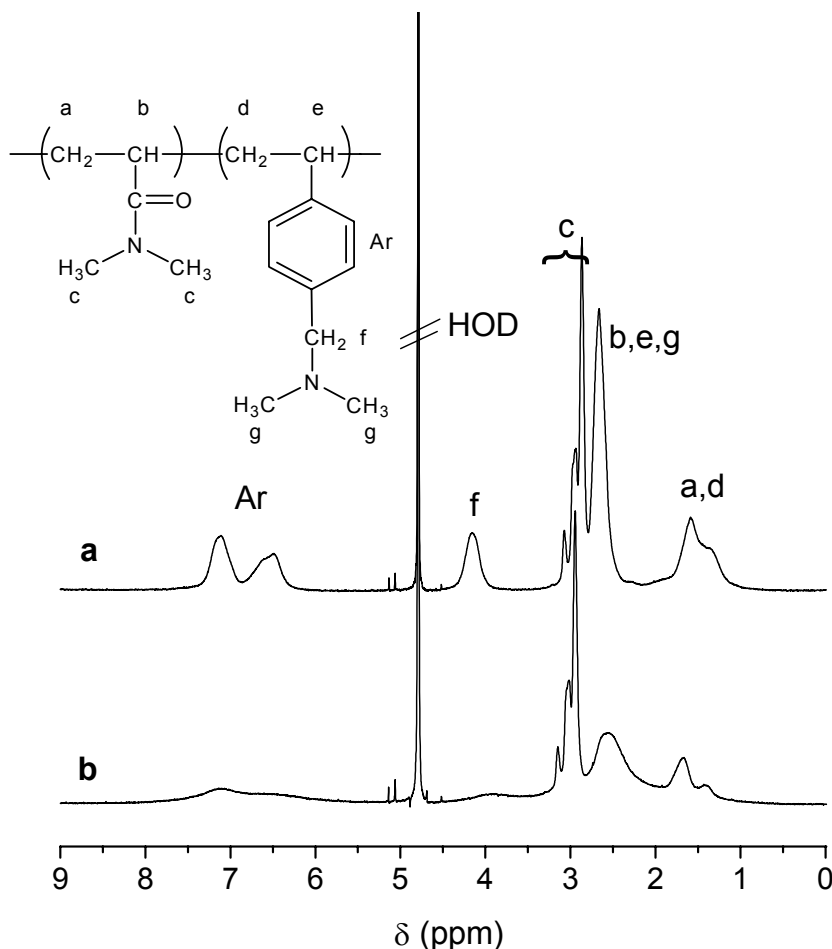


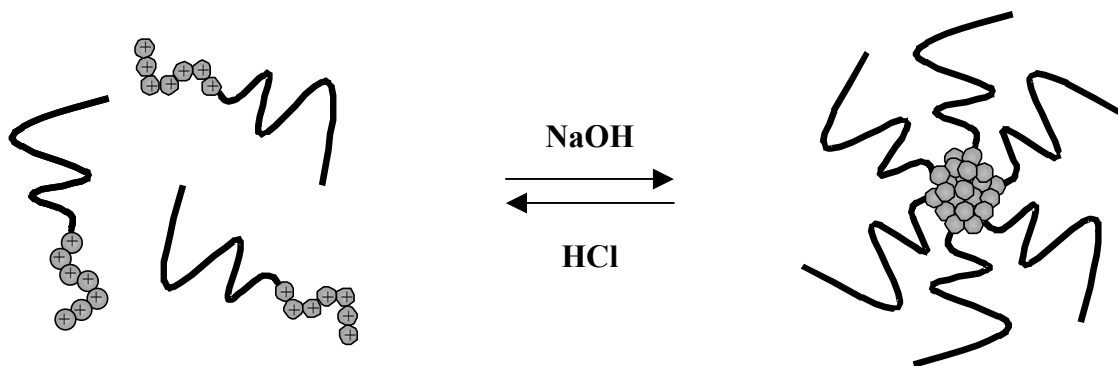
Figure 5. 300 MHz  $^1\text{H}$  NMR spectra and peak assignments for **P4** in  $\text{D}_2\text{O}$  at (a) pH 1 and (b) pH 10 (pH adjusted with DCl or NaOD).



### Solution Characterization

Due to the pH-insensitive nature of the DMA units, **P2-4** represent AB diblock copolymers that contain a constant length of a permanently hydrophilic A block, since the same homopolymer was employed as the macroCTA. PDMVBA homopolymer precipitates from aqueous solutions when the pH exceeds its  $pK_a$  ( $\sim 8.0$ ). This is due to a decreased degree of protonation which results in increased hydrophobicity. Thus, a DMA-DMVBA block copolymer should be hydrophilic-hydrophilic in acidic and neutral solutions and hydrophilic-hydrophobic under highly basic conditions. The length of the responsive DMVBA block was systematically varied in order to study the effects of copolymer composition on the self-assembly of the resulting copolymers as a function of pH.

Due to the stimuli-responsive behavior of the DMVBA block, no cosolvent was required to prepare micellar solutions. The block copolymers were first molecularly dissolved with sufficient HCl to ensure full protonation of the DMVBA units. The pH was then adjusted to  $1.0 \pm 0.3$ , and the solutions were filtered before being allowed to equilibrate with gentle agitation. Under these conditions the block copolymer should exist as single, isolated, molecularly dissolved chains, or “unimers”. The pH was then raised above the critical value ( $pH \approx pK_a$ ) at which point the DMVBA block became hydrophobic, and the block copolymer self-assembled forming micelle-like structures. (Scheme 3). The copolymer solutions were then titrated with NaOD to  $pH\ 10.0 \pm 0.2$  and allowed to equilibrate with gentle agitation to yield 0.5 w/v % micellar solutions.



*Scheme 3.* Reversible micellization of P(DMA-*b*-DMVBA) block copolymers as a function of solution pH.

$^1H$  NMR spectroscopy was employed to study the micellization behavior of the block copolymers in  $D_2O$ . Figure 5 shows the spectra for a 0.5 w/v % solution of **P4** at pH 1 and 10. The signals associated with the DMVBA units ( $\delta = 1.36, 1.58, 2.64, 4.14, 7.55-6.10$  ppm) diminish noticeably with an increase in solution pH. This is consistent with deprotonation of tertiary amine groups leading to dehydration of the DMVBA block followed by supramolecular self-assembly. In the micelle core, segmental mobility is severely restricted causing those NMR peaks associated with DMVBA to excessively broaden. The DMA signals persist, as would be expected since PDMA remains hydrophilic, even at very high pH.

DLS was then employed to characterize 0.5 w/v % solutions of the copolymers in water at pH 1 and 10 (Table 3). Under acidic conditions, there should be no aggregation. Indeed, the intensity-average hydrodynamic diameters ( $D_h$ ) obtained at low pH are in the range expected for molecularly dissolved polymers with the molecular weights considered, i.e 5-6 nm. A marked increase in  $D_h$  at pH 10 is observed for the block copolymer systems ( $D_h$  = 22-69 nm). These results, coupled with those obtained by  $^1\text{H}$  NMR spectroscopy, are consistent with the formation of polymeric micelles with hydrophilic DMA coronas and dehydrated DMVBA cores. Additionally, the micelle diameters increase with increasing length of the DMVBA block. This would be expected since the hydrophobic block controls the association behavior of amphipathic block copolymers in aqueous solutions.<sup>28</sup>

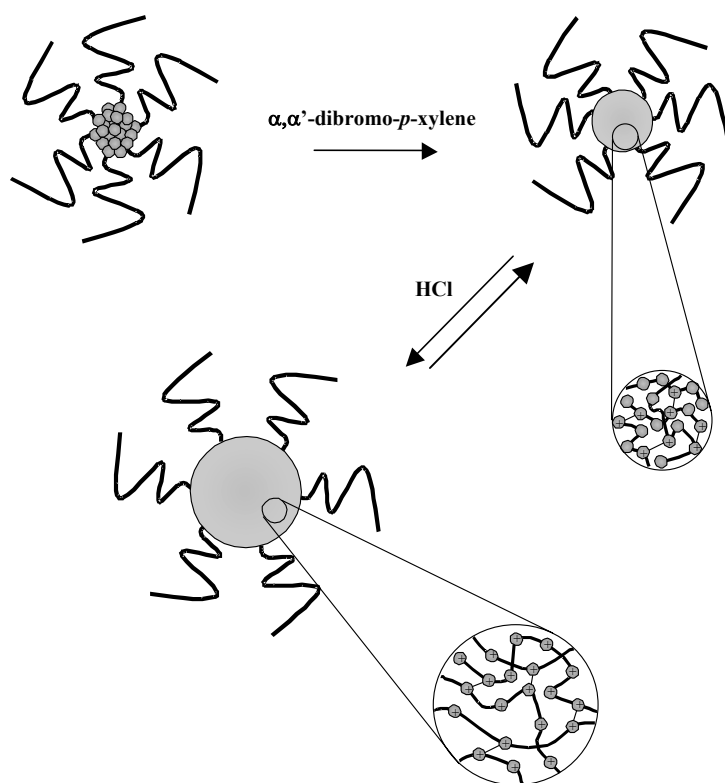
Table 3. Hydrodynamic Diameter ( $D_h$ ) and Polydispersity ( $\rho$ ) Determined by DLS at pH 1.0 and 10.0 for the PDMA MacroCTA and Block Copolymers with DMVBA.

	$D_h$ (nm)		
	pH 1.0	pH 10.0	$\rho$
<b>PDMA MacroCTA</b>	3	4	0.06
<b>P2</b>	5	22	0.16
<b>P3</b>	6	50	0.11
<b>P4</b>	6	69	0.14
<b>P3X</b>	101	59	0.18

In addition to providing pH-responsive behavior, the tertiary amine groups of the DMVBA block can also be utilized to selectively crosslink the core of the polymeric micelles (Scheme 4).<sup>29-31</sup> As a representative example, **P3** micelles were crosslinked by the addition of  $\alpha,\alpha'$ -dibromo-*p*-xylene. Due to its inherent hydrophobicity, the crosslinking agent should partition into the micelle cores, thus facilitating the potential for intermolecular linkage between the tertiary amine groups of adjacent chains.

In core-crosslinking reactions in which no charge is developed, a slight decrease in micelle size would be expected due to the core adopting a more compact morphology. However, the crosslinking reaction of **P3** (to give **P3X**) is accompanied by an increase in  $D_h$  from 50 to 59 nm. This is attributed to swelling of the micellar core due to enhanced hydration and coulombic repulsions between the positive charges that result from quaternization of the 3<sup>o</sup> amine groups. This hypothesis was corroborated by  $^1\text{H}$  NMR spectroscopy. Figure 6 shows the aromatic regions for the spectra of **P3** at pH 1 and 10 and **P3X** at pH 10. Since the spectra were normalized for block copolymer concentration, the difference in peak intensities implies that the degree of hydration of the DMVBA units of **P3X** at pH 10 is intermediate to those of **P3** at pH 1 and 10. In other words, the crosslinking reaction leads to an increased degree of hydration of the micelle

core, but segmental motion of the DMVBA block is still significantly restricted as compared to that of the fully dissociated unimers.



*Scheme 4.* Preparation and behavior of P(DMA-*b*-DMVBA) core-crosslinked micelles.

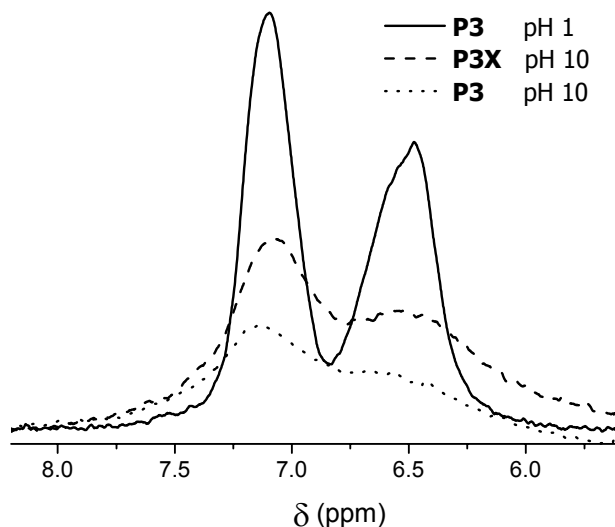
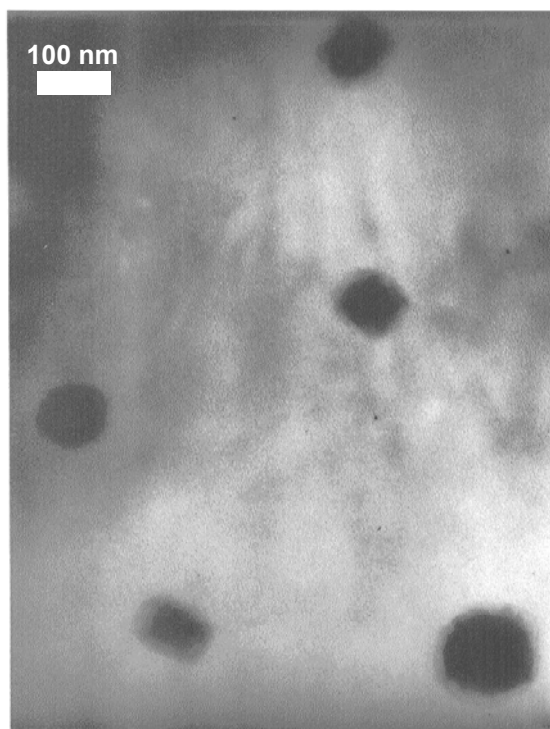


Figure 6. Aromatic region of  $^1\text{H}$  NMR spectra of **P3** at pH 1 and 10, and **P3X** at pH 10.

Due to intermolecular covalent bonding between core chains, crosslinked micelles are not capable of dissociating to their respective unimeric states. Contrary to the results observed for **P2-4**, when **P3X** is subjected to acidic conditions, a drastic *increase* in  $D_h$  is observed by DLS. For the non-crosslinked species conditions lead to molecular dissolution to the unimeric state, however, the crosslinked micellar chains are no longer able to dissociate. The increase in size again can be attributed to swelling of the micellar core from protonation of the tertiary amine groups (Scheme 4).

The core-crosslinked micelles were also visualized by TEM (Figure 7). A solution of **P3X** at pH 1 was cast onto a carbon-coated grid. If the micelle structure were not covalently linked, only unimers would be present under these conditions. Thus, the presence of the well-defined supramolecular aggregates on the order of 100 nm is further evidence for the successful cross-linking of the micelle cores.



*Figure 7.* TEM image of P(DMA-*b*-DMVBA) core-crosslinked micelles (**P3X**).

## CONCLUSIONS

The synthesis and solution characterization of a novel series of AB diblock copolymers with neutral, water-soluble acrylamido-based A blocks (DMA) and pH-responsive styrenic B blocks (DMVBA) have been accomplished. To our knowledge, this represents the first example of an acrylamido-styrenic block copolymer prepared in homogeneous aqueous solution. In order to yield well-defined block copolymers of DMA and DMVBA with minimal homopolymer impurity, it is necessary to polymerize DMA first and use this as a macroCTA for the block copolymerization of DMVBA. Due to the stimuli-responsive nature of the DMVBA block, reversible aggregation of these block copolymers was demonstrated using both  $^1\text{H}$  NMR spectroscopy and dynamic light scattering.

An example of core-crosslinked micelles was also obtained by the addition of a difunctional crosslinking agent to a micellar solution of the block copolymer. A slight increase in the micelle size was observed at high pH due to increased hydrophilicity of the core resulting from amine quaternization during cross-linking. The cross-linked micelles remain as intermolecular aggregates at low pH and actually increase in size due to complete protonation of the amine functionalities of the DMVBA block.

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