Direct Controlled Polymerization of a Cationic Methacrylamido Monomer in Aqueous Media via the RAFT Process†

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ABSTRACT: Controlled radical polymerization (CRP) combines the benefits of the robust nature of conventional radical polymerization with the ability to prepare advanced macromolecular architectures common to living polymerization techniques. Of the major CRP techniques, the reversible addition−fragmentation chain transfer (RAFT) technique appears to be the most tolerant of aqueous reaction conditions and a variety of monomer functionalities. To date, however, there have been no reports of the RAFT polymerization of a cationic (meth)acrylamido monomer directly in aqueous media. Herein we report the polymerization of *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMA) directly in aqueous media utilizing 4-cyanopentanoic acid dithiobenzoate (CTP) as the chain transfer agent (CTA). Polymerization in water at neutral pH allowed a moderate level of control over the polymerization up to 50% conversion. Polymerization in an aqueous buffer (pH = 5), on the other hand, afforded excellent control up to 98% conversion (M_n = 38 000, M_w/M_n = 1.12). Purification of the poly(DMAPMA) macro-CTA under conditions that minimize the exposure of the macro-CTA to an unbuffered aqueous environment was necessary for the retention of functional chain ends. Block copolymers of DMAPMA and *N*,*N*-dimethylacrylamide (DMA) or (*ar*-vinylbenzyl)trimethylammonium chloride (VBTAC) were successfully prepared from a macro-chain-transfer agent (macro-CTA) of poly(DMAPMA).

Introduction

Polymethacrylamides, a well-known class of water-soluble polymers widely used in industry and medicine, are known to polymerize by a variety of techniques, the most convenient of which is free radical polymerization. Traditional free radical polymerization, however, generates polymers with broad molecular weight distributions and relatively high molecular weight. For applications requiring better defined (co)polymers (low polydispersity, predetermined molecular weight, well-defined blocks, grafts, stars, etc.), living radical polymerization techniques such as atom transfer radical polymerization (ATRP),[1,2] nitroxide-mediated polymerization (NMP),[3,4] and reversible addition−fragmentation chain transfer polymerization (RAFT)[5−7] have been utilized.

The RAFT procedure has proven quite versatile from a synthetic viewpoint since a wide range of monomer classes, functional groups, and reaction conditions can be tolerated. For this reason, our group[8−18] and others[19−29] have focused on employing RAFT in the controlled polymerization of water-soluble acrylamido monomers. To date, the controlled RAFT polymerizations of anionic,[9,17,28] zwitterionic,[13,18,26] and neutral[10−12,15,18,19−27,29] acrylamido monomers have been reported. Polymerization of anionic acrylamides, sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) and sodium 3-acrylamido-3-methylbutanoate (AMBA), proceeded with excellent control and allowed the synthesis of AB and BA block copolymers (M_n = 69 700 and 57 900, M_w/M_n = 1.14 and 1.16, respectively).[9,17] Morishima and co-workers recently performed block copolymerizations of sodium 6-acrylamidohexanoate in water utilizing poly(AMPS) as a macro-chain-transfer agent (macro-CTA) also with excellent results.[28] The zwitterionic monomer 3-[2-(*N*-methylacrylamido)ethyldimethylammonio]propanesulfonate (MAEDAPS) has been used to prepare homopolymers and diblock and triblock copolymers with well-controlled molecular weight and low polydispersity (1.08−1.25).[13,18] Neutral substituted acrylamides include the monosubstituted, *N*-isopropylacrylamide (NIPAM),[20,21,23,25,26] and the bisubstituted acrylamides, *N*,*N*-dimethylacrylamide (DMA),[10−12,18−20,29] and *N*-acryloylmorpholine.[24,27] Recently, the RAFT polymerization of acrylamide itself was achieved directly in aqueous media through the use of an acidic buffer (M_n = 18 600, M_w/M_n = 1.06).[15]

Significantly, however, two classes of water-soluble monomers that remain underrepresented in the controlled free radical literature are the methacrylamido and cationic monomers. ATRP was used to polymerize *N*-(2-hydroxypropyl)methacrylamide.[30,31] Methyl 2-chloropropionate as an initiator and tris(2-dimethylaminoethyl)amine as a ligand in ethanol provided a well-defined polymer (M_n = 4480, M_w/M_n = 1.29); however, the conversion was limited due to the deactivation of the catalyst.[31] Other groups have turned to postmodification reactions of narrow molecular weight precursors poly(*N*-methacryloxysuccinimide)[32] and poly(*N*-acryloylsarcosine methyl ester)[33] with substituted amines to form statistical methacrylamido copolymers of controlled molecular weight.

Although a number of cationic monomers or their nonionic precursors have been polymerized by NMP[34−42] and ATRP,[43−58] only a few have been polymerized via RAFT to date. Reports of the RAFT polymerization of cationic monomers include the polymerization of (*ar*-vinylbenzyl)trimethylammonium chloride (VBTAC),[8,59] *N*,*N*-dimethylvinylbenzylamine,[8,59] and 2-(dimethylamino)ethyl methacrylate.[5,19] More recently, the RAFT

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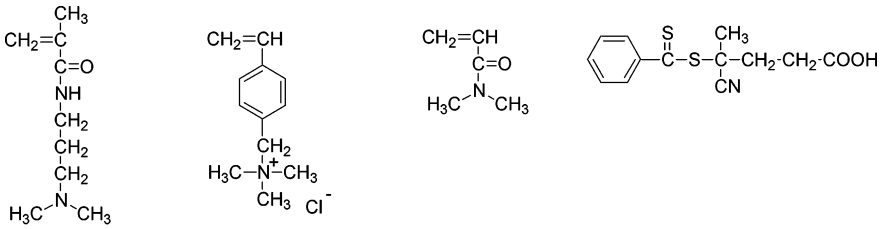


Figure 1. Structures and acronyms of monomers and the CTA utilized in polymerization.

polymerization of vinylpyridines has been reported.[16] To our knowledge, however, no direct polymerization via RAFT of a (meth)acrylamido monomer bearing an amino group has been previously reported.

In this paper we detail the facile preparation of well-defined block copolymers containing *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPMA) directly in aqueous media utilizing 4-cyanopentanoic acid dithobenzoate (CTP) as the CTA. First, the influence of the reaction medium and initiator concentration on the kinetic features of the process was studied to allow the optimization of the polymerization conditions. A DMAPMA macro-CTA was then employed in a subsequent blocking reaction with DMA or VBTAC. For comparison, block copolymerizations of DMAPMA utilizing macro-CTAs of DMA and VBTAC were also attempted.

Experimental Section

Materials. All chemicals were purchased from Aldrich at the highest available purity and used as received unless otherwise noted. 4,4′-Azobis(4-cyanopentanoic acid) (V-501, a gift from Wako Pure Chemicals Industries, Ltd.) was recrystallized from methanol. *N*-[3-(Dimethylamino)propyl]methacrylamide (DMAPMA) and *N*,*N*-dimethylacrylamide (DMA) were distilled over calcium hydride immediately prior to polymerization (Figure 1). Deionized water (DI H_2O) was obtained from a Barnstead NANO-Pure reverse osmosis/filtration unit (resistivity 18.0 MΩ). Poly(2-vinylpyridine) standards were purchased from Polysciences Inc.

Synthesis of 4-Cyanopentanoic Acid Dithiobenzoate. 4-Cyanopentanoic acid dithiobenzoate (CTP) was synthesized according to the literature procedure[8] utilizing a small amount of acetic acid (0.5% v/v) in the chromatographic eluent to enhance chromatographic resolution.

Polymerization. Homopolymerization of *N*-[3-(Dimethylamino)propyl]methacrylamide. The following two examples illustrate the general synthetic protocols employed.

Homopolymerization in Water. DMAPMA (3.41 g, 0.020 mol) was dissolved in water at 0 °C, and the pH of the solution was adjusted to 6.85 with concentrated HCl(aq). Aqueous solutions of CTP (19.03 mg, 0.068 mmol) and V-501 (2.39 mg, 0.0085 mmol) were prepared by neutralization with aqueous NaOH and added to the monomer solution, resulting in a final solution pH = 7. Reactions were carried out in a round-bottom flask equipped with a magnetic stir bar and sealed by a rubber septum. Polymerization solutions were degassed by purging with nitrogen for 20 min and allowed to react at 70 °C. Aliquots for kinetic analysis were removed from the polymerization solution after appropriate intervals.

Homopolymerization in Buffer. DMAPMA (3.41 g, 0.020 mol) was dissolved in 1.6 mL of buffer (pH = 5, 0.27 mol/L acetic acid and 0.73 mol/L sodium acetate) at 0 °C, and the pH of the solution was adjusted to 5 with HCl. CTP (19.03 mg, 0.068 mmol) and initiator (2.39 mg, 0.0085 mmol) were added, and the solution was diluted to 10 mL volume with the buffer solution. Polymerization solutions were degassed by purging with nitrogen for 20 min and allowed to react at 70 °C. Aliquots for kinetic analysis were removed from the polymerization solution after appropriate intervals.

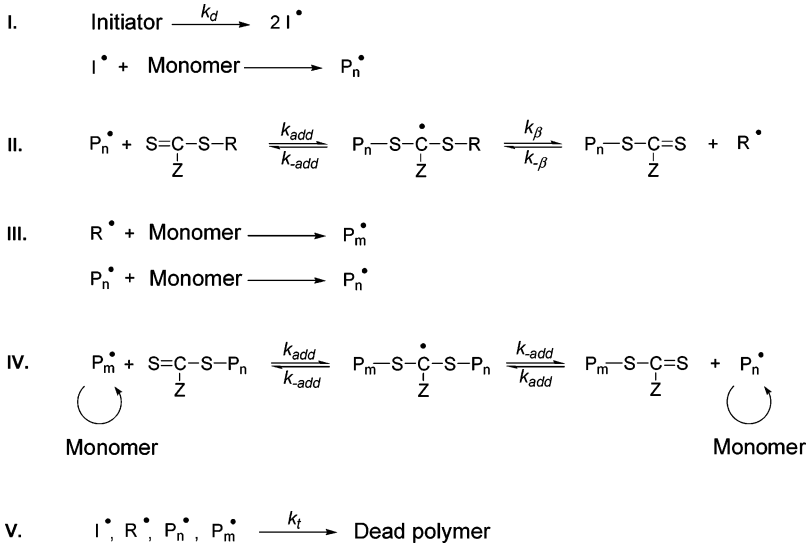
Synthesis of Poly(*N*-[3-(dimethylamino)propyl]methacrylamide) Macro-CTA (Macro-DMAPMA). DMAPMA (3.41 g, 0.020 mol) was dissolved in 1.6 mL of acetic acid/sodium acetate buffer at 0 °C, and the pH of the solution was adjusted to 5 with HCl. CTP (19.03 mg, 0.068 mmol) and initiator (2.39 mg, 0.0085 mmol) were added based on a target M_n = 20 300, and the solution was diluted to 10 mL with the buffer solution. Polymerization solutions were degassed by purging with nitrogen for 20 min and allowed to react at 70 °C for 60 min until 24% conversion. After polymerization, the reaction solution was poured into acetone to precipitate the polymer (polymerization solution/acetone = 1/20 (v/v)). The polymer was then redissolved in DI H_2O and precipitated a second time into acetone. Finally, the polymer was dissolved in DI H_2O and purified by ultrafiltration in a Centra-GP8 ventilated centrifuge (Thermo IEC) using a Macrosep centrifugal device (3000 MWCO). Lyophilization afforded 1.56 g (78.77% yield) of the desired macro-CTA as a bright pink powder. ^{1}H NMR (300 MHz, 0.096 M NaCl D_2O with 23.5 wt % DCl): δ 0.45−1.18 (br, 2H, CH_2C), 1.52−2.05 (br, 3H, CCH_3), 2.65−3.41 (br, 12H, CONHCH_2CH_2CH_2, NCH_3). ^{13}C NMR (300 MHz, 0.096 M NaCl D_2O with 23.5 wt % DCl): δ 19.7 (CCH_3), 26.0 (CONHCH$_2$CH_2), 39.8 (CH_2C), 45.6 (NCH_3), 47.7 (CH$_2$C), 58.1, 60.6 (CONHCH_2CH$_2$CH_2), 181.6 (C═O).

Synthesis of Poly(*N*,*N*-dimethylacrylamide) Macro-CTA (Macro-DMA). Macro-DMA was synthesized in water using CTP as the CTA and V-501 as the initiator.[12] DMA (5.35 g, 0.054 mol) and CTP (37.39 mg, 0.134 mmol) were dissolved in 28 mL of acetic acid/sodium acetate buffer (target M_n = 40 300). V-501 (7.50 mg, 0.0268 mmol) was added, and the solution was diluted to 30 mL volume with the buffer solution. Polymerization solutions were degassed by purging with nitrogen for 20 min and allowed to react at 80 °C for 20 min until 23% conversion. Purification was achieved by dialysis against DI H_2O with 1000 MWCO dialysis tubing (Spectrapor) followed by lyophilization to give 1.19 g (96.73%, yield) of macro-CTA. ^{1}H NMR (300 MHz, 0.096 M NaCl D_2O with 23.5 wt % DCl): δ 1.21−1.96 (br, 2H, CH_2), 2.29−3.32 (br, 7H, CH, CH_3). ^{13}C NMR (300 MHz, 0.096 M NaCl D_2O with 23.5 wt % DCl): δ 36.1−41.6 (CH, CH_2, CH_3), 178.1 (C═O).

Synthesis of Poly((*ar*-vinylbenzyl)trimethylammonium chloride) Macro-CTA (Macro-VBTAC). Macro-VBTAC was prepared according to a literature procedure using CTP as the CTA and V-501 as the initiator.[8] VBTAC (5.08 g, 0.024 mol) and CTP (70.99 mg, 0.254 mmol) were dissolved in 28 mL of acetic acid/sodium acetate buffer (target M_n = 20 300). V-501 (14.24 mg, 0.0508 mmol) was added, and the solution was diluted to 30 mL volume with the buffer solution. Polymerization solutions were degassed by purging with nitrogen for 20 min and allowed to react at 70 °C for 100 min until 85% conversion. Macro-VBTAC was purified by dialysis against DI H_2O with 1000 MWCO dialysis tubing followed by lyophilization to give 4.06 g (94.07% yield) of polymer. ^{1}H NMR (300 MHz, 0.096 M NaCl D_2O with 23.5 wt % DCl): δ 0.54−3.05 (br, 12H, CH_2CH, CH_3), 3.58−4.76 (br, 2H, NCH_2), 5.91−7.33 (br, 4H, ArH). ^{13}C NMR (300 MHz, 0.096 M NaCl D_2O with 23.5 wt % DCl): δ 43.2 (CH_2CH), 54.9 (CH_3), 71.4 (NCH_2), 127.1, 131.2, 135.0, 150.7 (ArC).

Synthesis of Diblocks. The block copolymers poly(DMAPMA-*b*-DMAPMA), poly(DMA-*b*-DMAPMA), and poly(VBTAC-*b*-DMAPMA) were synthesized according to the gen-

Scheme 1. Proposed RAFT Mechanism



eral procedure for DMAPMA in an acetic acid/sodium acetate buffer using the appropriate macro-CTA instead of CTP. For instance, DMAPMA (1.70 g, 0.010 mol) was dissolved in 0.8 mL of acetic acid/sodium acetate buffer at 0 °C, and the pH of the solution was adjusted to 5 with HCl. Macro-DMA (0.42 mg, 0.034 mmol) and V-501 (1.91 mg, 0.0068 mmol) were added, and the solution was diluted to 5 mL volume with the buffer solution. Polymerization solutions were degassed by purging with nitrogen for 20 min and allowed to react at 80 °C for 30 min until 40% conversion.

The diblock polymers poly(DMAPMA-*b*-DMA) and poly(DMA-*b*-DMA) were prepared under the conditions described for the preparation of macro-DMA using the appropriate macro-CTA as the chain transfer agent instead of CTP and a buffer solution instead of DI H_2O. The diblock polymers poly(DMAPMA-*b*-VBTAC) and poly(VBTAC-*b*-VBTAC) were prepared under the conditions described for macro-VBTAC using the appropriate macro-CTA instead of CTP and an acetic acid/sodium acetate buffer instead of DI H_2O. For instance, VBTAC (2.72 g, 0.016 mol) and macro-DMAPMA (0.32 g, 0.054 mmol) were dissolved in 7 mL of acetic acid/sodium acetate buffer. V-501 (3.05 mg, 0.0109 mmol) was added, and the solution was diluted to 8 mL volume with the buffer solution. Polymerization solutions were degassed by purging with nitrogen for 20 min and allowed to react at 70 °C for 180 min until 94% conversion.

After polymerization, the pH of the solutions was adjusted to 12.5 with 1 N NaOH(aq) before dialysis against DI H_2O with 1000 MWCO dialysis tubing followed by lyophilization, affording a quantitative yield. For polymers containing a VBTAC block, dialysis for 2 days in 2 N NaCl solution was required to fully ion exchange the cationic block to the chloride form before dialysis in DI H_2O.

Analytical Techniques. Aqueous Size Exclusion Chromatography (ASEC). Average molar masses and polydispersities in poly(2-vinylpyridine) equivalents were determined by ASEC, using SynChropak CATSEC columns (100, 300, and 1000 Å; Eichrom Technologies Inc.) and 1 wt % acetic acid/0.1 M Na_2SO_4(aq) as the eluent at a flow rate of 0.3 mL/min. Detection was achieved with a Spectra-Physics UV2000 detector and a Knauer K-2301 RI detector at ambient temperature. The consumption of monomers was determined by comparing the area of the UV signal of the monomer peak to the area at time zero. The absolute molecular weights and polydispersities of poly(DMAPMA) were determined by ASEC at ambient temperature using SynChropak CATSEC columns (100, 300, and 1000 Å; Eichrom Technologies Inc.), a Polymer Labs LC1200 UV/vis detector, a Knauer K-2301 RI detector (λ = 950 nm), a Wyatt DAWN DSP multiangle laser light scattering detector (λ = 633 nm), and 1 wt % acetic acid/0.1 M Na_2SO_4-(aq) as the eluent at a flow rate of 0.3 mL/min. The d*n*/d*c* of poly(DMAPMA) (0.194 mL/g) in the above eluent was determined at 25 °C with a Knauer K-2301 RI detector (λ = 950 nm).

The absolute molecular weights and polydispersities of macro-DMA and poly(DMA-*b*-DMA) were determined by ASEC/MALLS using Viscotek TSK Viscogel columns (G3000PW_{XL} (200 Å) and G4000PW_{XL} (500 Å), Polymer Labs LC1200 UV/vis detector, Wyatt Optilab DSP interferometric refractometer (λ = 690 nm), a Wyatt DAWN EOS multiangle laser light scattering detector (λ = 690 nm), and 0.05 M Na_2SO_4/acetonitrile, 80/20 (v/v), solution as an eluent with a flow rate of 0.5 mL/min at ambient temperature. The d*n*/d*c* = 0.1645 for poly(DMA) at 25 °C in the above eluent was obtained from the literature.[12]

Other Measurements. All pH measurements were performed with accuracy ±0.02 with 900A (Orion) pH meter. ^{1}H and ^{13}C NMR spectra were recorded with a Varian Mercury^{PLUS} 300 MHz spectrometer with a delay time of 5 s in a 0.096 M NaCl/D_2O solution containing 23.5 wt % DCl. Chemical shifts were determined by using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS) as an internal reference. Gated proton-decoupled ^{13}C NMR spectroscopy, with delay time of 5 s, was used to determine the copolymer composition of poly(DMAPMA-*b*-DMA) by integration of the relative intensities of carbonyl peaks at 181.6 ppm (macro-DMAPMA) and 178.1 ppm (poly(DMA)).

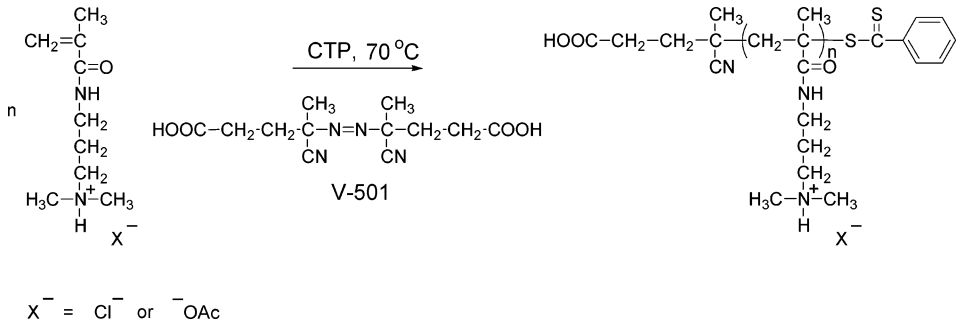
Results and Discussion

Homopolymerization of DMAPMA in Water. It has been demonstrated that successful implementation of the RAFT process requires careful selection of the CTA and reaction conditions for the monomer of interest.[11,12,15,60−62] The Z-group (Scheme 1) stabilizes the intermediate radical and promotes addition to the C═S bond. The R-group should be chosen so that fragmentation of the intermediate radical is facile, and the expelled radical R• has sufficient potential energy to reinitiate polymerization.

In our previous work, we have shown that the polymerization of a wide range of acrylamido monomers may be controlled utilizing CTP as the CTA.[9,12,13,17,18] CTP is particularly well suited for aqueous polymerization due to the presence of the carboxylate moiety on the R-group which imparts water solubility. For these reasons we chose to investigate CTP in the RAFT polymerization of the protonated form of DMAPMA.

DMAPMA polymerizations were performed in aqueous solution at 70 °C using V-501 as the initiator with

Scheme 2. Overall Scheme for the RAFT Polymerization of DMAPMA



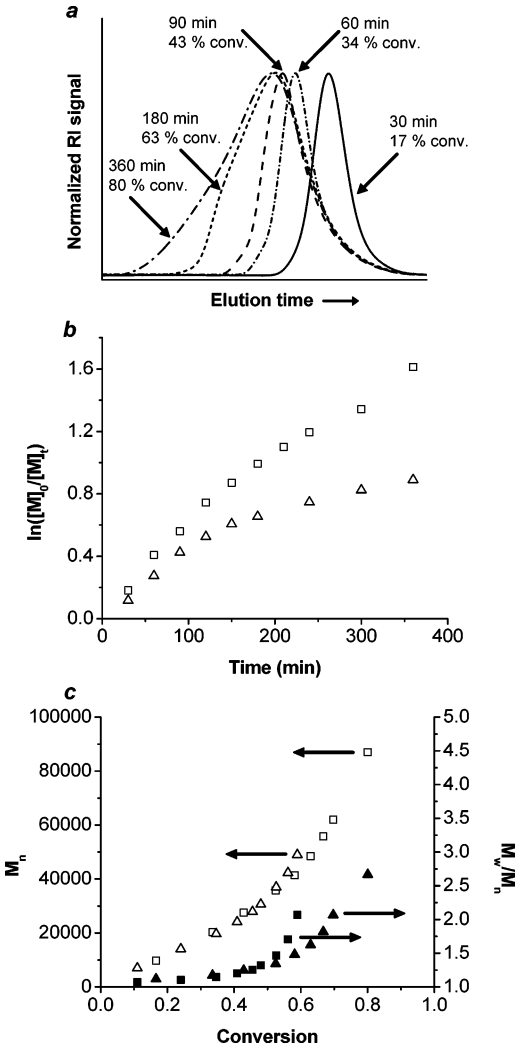


Figure 2. (a) ASEC traces of poly(DMAPMA) ([CTA]/[I] = 5/1), (b) pseudo-first-order kinetic plots, and (c) dependence of M_n (open symbols) and M_w/M_n (solid symbols) on the monomer consumption in the polymerization of DMAPMA in water, pH = 7, at 70 °C: [CTA]/[I] = 5/1 (squares) and [CTA]/[I] = 8/1 (triangles).

[CTA]/[I] ratios of 5/1 and 8/1 (Scheme 2). To avoid CTA hydrolysis in basic conditions (pK_a of DMAPMA = 9.25[63]), the pH of the solution was adjusted to 7 with concentrated HCl. The ASEC traces of poly(DMAPMA) prepared with [CTA]/[I] = 5/1 at selected reaction times are presented in Figure 2a (the traces for 8/1 ratio were similar). Unimodal peaks were observed at decreasing elution times as normally evidenced for a "living"/controlled polymerization. After 180 min, however, a high molecular weight shoulder appeared, suggesting the presence of termination events at longer reaction times.

As shown in Figure 2b, the pseudo-first-order kinetic plots are linear over the first 180 min, after which downward curvature is observed. This plot is expected to be linear only if the kinetics are first-order with respect to the monomer and the concentration of active species remains constant. Since there is no reason to suspect a higher order dependence of the polymerization rate on monomer concentration, a decrease in the concentration of propagating radicals may be inferred.

The evolution of molecular weight with monomer conversion (Figure 2a,c) exhibits linearity up to 50% conversion, indicating well-controlled polymerization up to that point; however, at longer reaction times, a substantial positive deviation from linearity occurs. The broadening of the chromatograms continues with reaction time, increasing to $M_w/M_n = 2.67$ for the polymerization with [CTA]/[I] = 5/1. Additionally, comparison of the absolute and theoretical molecular weights (Table 1) reveals substantial deviation.

It should be noted that no induction period is evident for the polymerization of DMAPMA in the presence of CTP. Previously, induction periods of 20−60 min were observed for the polymerization of DMA,[12] AMPS,[9] AMBA,[9] and MAEDAPS[13] under similar conditions. The absence of an induction period indicates that fragmentation and reinitiation are more closely matched for the methacrylamido-CTP pair than the acrylamido-CTP pair.[11,64] This result is not unexpected due to the greater structural similarity between the CTP R-group and the poly(DMAPMA) chain end (both leaving groups are tertiary) and further confirms earlier results.[11,64]

Homopolymerization of DMAPMA in Buffer. In a previous publication, we showed that the polymerization of acrylamide was substantially improved by performing the polymerization in an acetic acid/sodium acetate buffer (pH = 5).[15] Monomer hydrolysis, followed by attack of ammonia on the dithioester bond of the CTA, was proposed as the failure mechanism at neutral solution pH values. At low solution pH values, protonation of the resulting ammonia inhibited aminolysis.[65] Considering the possibility of DMAPMA hydrolysis,[66] we sought to improve the RAFT polymerization of DMAPMA by performing the RAFT polymerization under similar conditions. The ASEC traces of poly(DMAPMA) obtained in the buffer solution at selected reaction times ([CTA]/[I] = 1.5/1) are presented in Figure 3a. Narrow unimodal peaks are observed throughout most of the reaction. Only at very high conversion (over 85%) does a small, high molecular weight shoulder appear, indicating some termination; however, the polydispersity remained very low ($M_w/M_n = 1.12$) even at 98% conversion. The kinetic data for polymerizations

Table 1. Kinetic and Molecular Weight Data for the RAFT Polymerization of DMAPMA Using CTP as a CTA and V-501 as an Initiator in Aqueous Media at 70 °C[a]

sample	solvent	[CTA]/[I]	time (min)	conv[b] (%)	$M_{n,MALLS}$[c]	$M_{n,th}$[d]	M_w/M_n[b]
DMAPMA1	DI H_2O	5	180	63	44 500	31 800	1.62
DMAPMA2	DI H_2O	8	180	48	33 300	24 300	1.32
DMAPMA3	buffer	1.5	180	93	47 100	46 800	1.08
DMAPMA4	buffer	3	180	81	37 700	40 800	1.07
DMAPMA5	buffer	5	180	68	32 400	34 300	1.06
DMAPMA6	buffer	8	180	55	28 100	27 800	1.07
DMAPMA7	buffer	*e*	60	10			

[a] [M] = 2 mol/L, [CTP] = 6.81×10^{-3} mol/L. [b] Determined by direct analysis of polymerization solutions by ASEC. [c] Molecular weight determined by ASEC/MALLS with 1 wt % acetic acid/0.1 M Na_2SO_4 aqueous solution as an eluent. [d] Calculated from conversion using eq 2. [e] No CTP; [V-501] = 2.27×10^{-3} mol/L, gellike after 60−90 min.

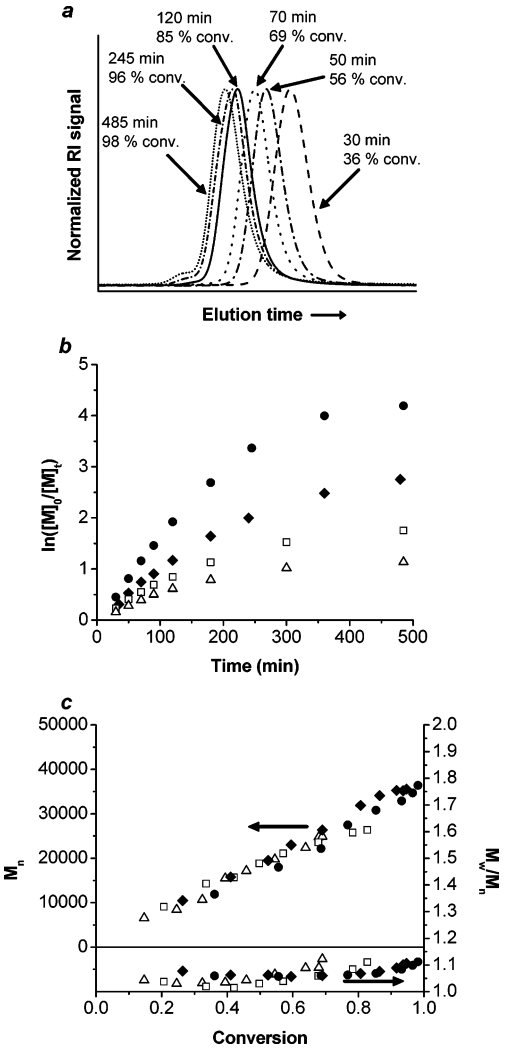


Figure 3. (a) ASEC traces of poly(DMAPMA) ([CTA]/[I] = 1.5/1), (b) pseudo-first-order kinetic plots, and (c) dependence of M_n and M_w/M_n on the monomer conversion in the polymerization of DMAPMA in an acetic acid/sodium acetate buffer, pH = 5, at 70 °C: [CTA]/[I] = 1.5/1 (circles), [CTA]/[I] = 3/1 (diamonds), [CTA]/[I] = 5/1 (squares), and [CTA]/[I] = 8/1 (triangles).

with different initiator concentrations and the linear increase in molecular weight with conversion are shown in parts b and c of Figure 3, respectively. Higher concentrations of initiator resulted in higher rates of polymerization due to an increase in the number of radicals available for propagation. After 180 min the conversion increased from 55% to 93%, and the number-average molecular weight increased from 19 800 to 32 900 as [CTA]/[I] decreased from 8 to 1.5 (Table 1).

Interestingly, no deterioration in the control of the polymerization was observed as the [CTA]/[I] decreased, with significant deviations from linearity in the pseudo-first-order plots occurring only at reaction times >250 min. Indeed, the higher rates of polymerization at [CTA]/[I] = 1.5/1 allowed 98% monomer conversion to be achieved under controlled conditions. Whatever the value of [CTA]/[I], polydispersities remained low (M_w/M_n < 1.12, Figure 3c), and the molecular weights vs conversion remained linear throughout the reaction in buffer. Further, the molecular weights determined by MALLS were in reasonable agreement with theoretical values (Table 1). This is in marked contrast to the high polydispersities (M_w/M_n = 2.07−2.67) and loss of molecular weight control observed in DI H_2O (Figure 2, Table 1).

The total number of chains in RAFT polymerization is determined by the number of CTAs that have successfully fragmented and reinitiated polymerization plus the number of initiator-derived chains. Thus, once all the CTA has been converted to macro-CTA, the theoretical molecular weight, $M_{n,th}$, can be obtained via eq 1.

$$M_{n,th} = \left(\frac{[M]_0 MW_{mon} p}{[CTA]_0 + 2f[I]_0(1 - e^{-k_d t})}\right) + MW_{CT} \quad (1)$$

Here $[M]_0$, MW_{mon}, p, $[CTA]_0$, f, $[I]_0$, k_d, t, and MW_{CTA} represent the initial monomer concentration, molecular weight of the monomer, conversion, initial CTA concentration, initiator efficiency, initial initiator concentration, rate constant for initiator decomposition, time, and the molecular weight of the CTA, respectively. When the initial CTA concentration is large compared to the number of initiator derived chains ($[CTA]_0 \gg 2f[I]_0(1 - e^{-k_d t})$), eq 1 can be simplified to eq 2.

$$M_{n,th} = \left(\frac{[M]_0 MW_{mon} p}{[CTA]_0}\right) + MW_{CTA} \quad (2)$$

For the buffered polymerizations in this work, the molecular weights of the polymers increased linearly with conversion, and the values were similar for equivalent conversions at all [CTA]/[I] ratios, indicating that the differences in $[I]_0$ had little effect on the total number of chains for these relatively short reaction times. Under these conditions the use of eq 2 is justified.

Copolymerization of DMAPMA in Buffer. Any living technique requires that each polymer chain retain an active end group (dithioester in this case). The presence of such a group provides unique opportunities for the preparation of block copolymers and more complex architectures (e.g., stars, etc.). To demonstrate

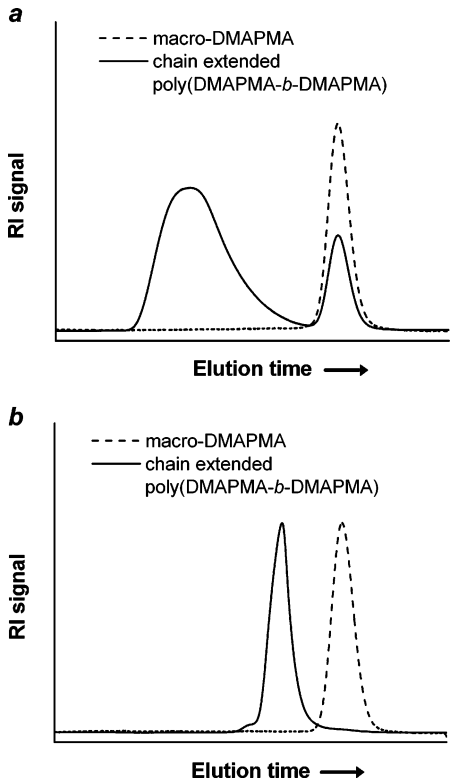


Figure 4. (a) ASEC traces of macro-DMAPMA (M_n = 11 300, M_w/M_n = 1.08) purified by dialysis and the unsuccessfully chain extended product and (b) macro-DMAPMA (M_n = 8800, M_w/M_n = 1.08) purified by precipitation and ultrafiltration and the chain extended product. All polymerizations were performed in an acetic acid/sodium acetate buffer [macro-DMAPMA]/[I] = 3/1, pH = 5, at 70 °C.

the retention of the dithioester group in DMAPMA polymerization, a macro-DMAPMA chain transfer agent was synthesized, isolated, and chain extended with DMAPMA. We found immediately that the purification procedure could have a profound effect on the blocking efficiency of the resulting macro-CTA. Initially macro-CTAs were purified by dialysis for 5 days against DI H_2O and lyophilized, yielding orange polymers. Macro-CTAs prepared in this manner exhibited poor blocking efficiency as seen in Figure 4a. However, when the purification procedure was modified to include two precipitations followed by ultrafiltration, a much higher self-blocking efficiency was observed (Figure 4b). It seems that, for poly(DMAPMA), extended exposure to unbuffered aqueous environment, even at room temperature, results in substantial loss of the dithioester moiety, presumably by dithioester hydrolysis.

Figure 5a presents the ASEC traces of the macro-DMAPMA (M_n = 8700, M_w/M_n = 1.08) used for the blocking experiments and the extended polymer poly(DMAPMA-*b*-DMAPMA) obtained within 180 min utilizing this macro-CTA. A shift of the distribution toward a higher molecular weight region clearly demonstrates efficient block formation. Some tailing can be seen, suggesting a small number of dead chains. A partial inactivation of the poly(DMAPMA) chains during homopolymerization and/or purification cannot, therefore, be neglected. Also, a minor high molecular weight shoulder suggests the presence of a small amount of bimolecular coupling.

The pseudo-first-order rate plot and the plot of M_n vs conversion for the chain extension of macro-DMAPMA purified by ultrafiltration are presented in parts b and

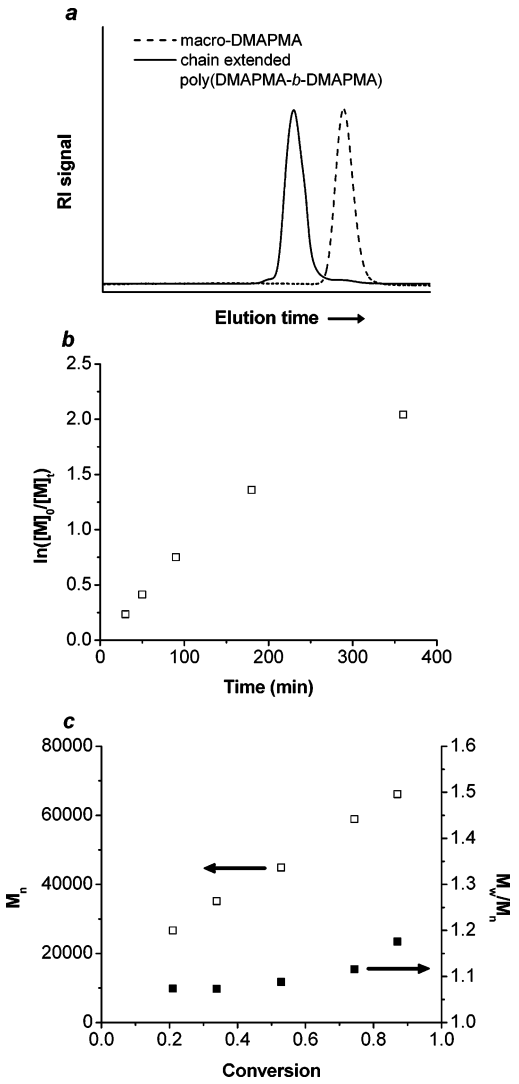


Figure 5. (a) ASEC traces of macro-DMAPMA (M_n = 8700, M_w/M_n = 1.08) purified by precipitation and ultrafiltration and the successfully chain extended polymer, 180 min, M_n = 58 900, M_w/M_n = 1.12), (b) pseudo-first-order kinetic plots, and (c) dependence of M_n (open symbols) and M_w/M_n (closed symbols) on the monomer consumption in the polymerization of DMAPMA in an acetic acid/sodium acetate buffer using a macro-DMAPMA as the chain transfer agent. [macro-DMAPMA]/[I] = 5/1, pH = 5, at 70 °C.

c of Figure 5, respectively. As expected, linearity of both plots is retained, and the kinetics of the chain extension are similar to that of the homopolymerization. The only significant difference is the positive intercept of the M_n vs conversion plot that cannot be entirely attributed to the molecular weight of the macro-CTA (intercept = 14 400, $M_{n,macro-CTA}$ = 8700). A positive *y*-intercept is known to occur when the rate of polymerization is greater than the rate of addition to CTA.[64] It is interesting that such a large *y*-intercept occurs for chain extension of macro-CTA when no significant intercept is observed for the homopolymerization (Figure 3c). Such an observation is consistent with a retarded rate of addition to the C=S bond for polymeric CTAs versus low molecular weight CTAs. This is under current investigation in our laboratories.

To further demonstrate the ability of DMAPMA to form AB diblock copolymers via RAFT, the synthesis of block copolymers with acrylamido (DMA) and styrenic (VBTAC) monomers was attempted (Scheme 3,

Scheme 3. Overall Scheme for Diblock Copolymerizations

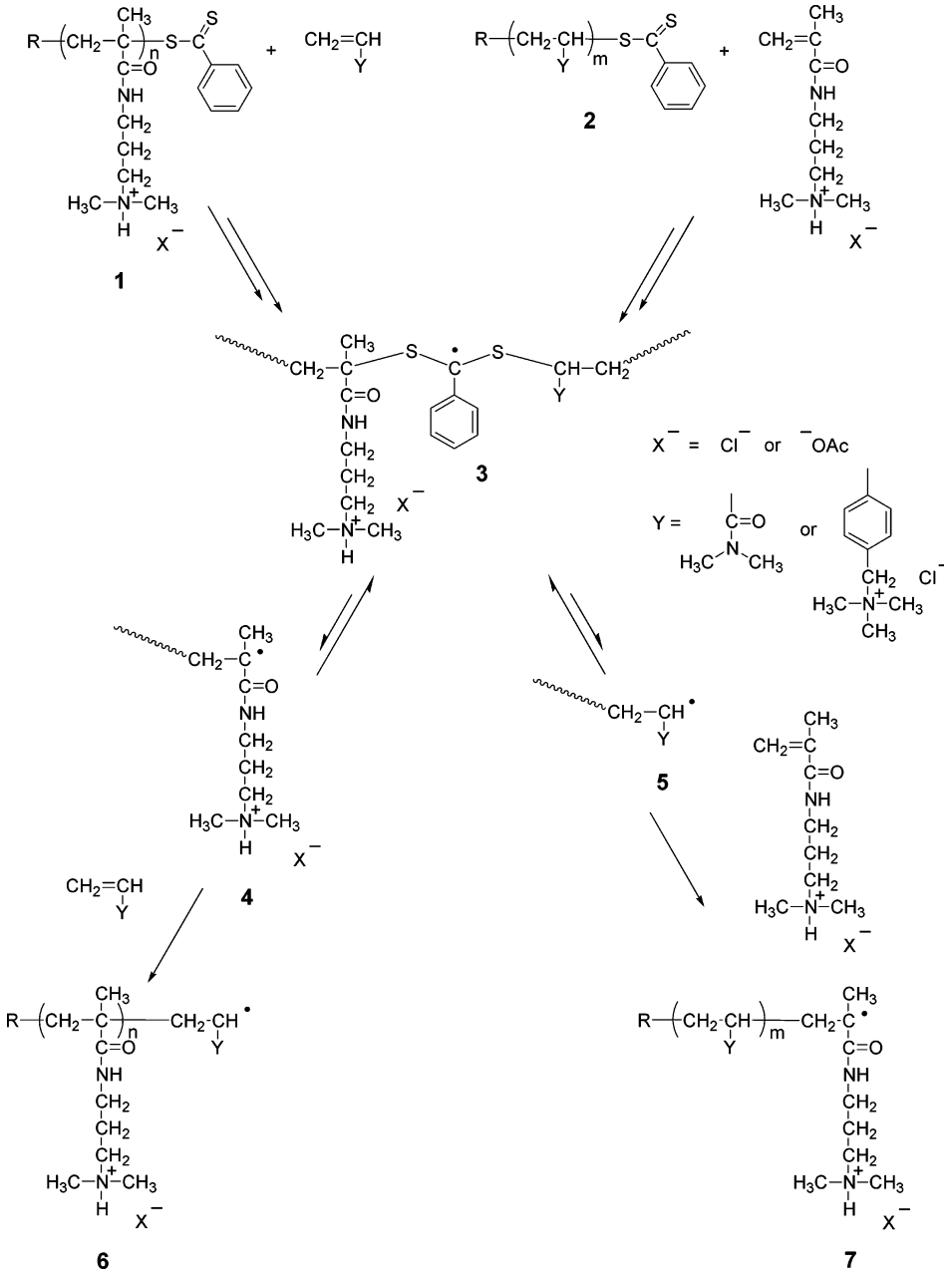


Table 2. Macromolecular Characteristics of Poly(DMAPMA), Poly(VBTAC), and Poly(DMA) Macro-CTAs and Corresponding Block Copolymers Obtained via RAFT in an Acetic Acid/Sodium Acetate Buffer (pH = 5)

sample	[CTA]/[I]	time (min)	conv[a] (%)	M_n[a]	M_w/M_n[a]	temp (°C)
macro-DMA[b,c]	5	20	23	8200 (12 200)[d]	1.08 (1.12)[d]	80
macro-VBTAC[c,e]	5	100	85	5800	1.08	70
macro-DMAPMA[f]	8	60	24	8700	1.08	70
poly(DMAPMA-*b*-DMAPMA)[g]	5	30	21	26 700	1.07	70
poly(DMA-*b*-DMAPMA)[g]	5	30	40	>540 000[h]		80
poly(VBTAC-*b*-DMAPMA)[g]	5	30	30	>540 000[h]		70
poly(DMA-*b*-DMA)[b]	5	20	21	18 300 (21 500)[d]	1.09 (1.06)[d]	80
poly(VBTAC-*b*-VBTAC)[e]	5	100	88	31 100	1.14	70
poly(DMAPMA-*b*-DMA)[b]	5	20	32	37 200	1.14	80
poly(DMAPMA-*b*-VBTAC)[e]	5	180	94	24 600	1.11	70

[a] Determined by ASEC as poly(2-vinylpyridine) equivalents in 1 wt % acetic acid/0.1 M Na_2SO_4 aqueous solution as the eluent. [b] [M] = 1.8 mol/L, [CTA] = 4.46×10^{-3} mol/L, [V-501] = 0.89×10^{-3} mol/L. [c] Solvent = water. [d] Absolute values determined by ASEC/MALLS in 0.05 M Na_2SO_4/acetonitrile, 80/20 v/v solution as the eluent. [e] [M] = 0.8 mol/L, [CTA] = 8.47×10^{-3} mol/L, [V-501] = 1.69×10^{-3} mol/L. [f] [M] = 2 mol/L, [CTA] = 6.81×10^{-3} mol/L, [V-501] = 0.85×10^{-3} mol/L. [g] [M] = 2 mol/L, [CTA] = 6.81×10^{-3} mol/L, [V-501] = 1.36×10^{-3} mol/L. [h] Eluted beyond the limits of the calibration.

Table 2). Reaction conditions utilizing [CTA]/[I] = 5/1 were chosen to more closely mimic previously reported conditions for DMA and VBTAC; however, all polymerizations were carried out in the acetate buffer found to be optimal for controlled DMAPMA polymerization. Results of the polymerizations of DMAPMA in the

presence of macro-DMA (M_n = 12 200, M_w/M_n = 1.12) and macro-VBTAC (M_n = 5800, M_w/M_n = 1.08) are presented in parts a and b of Figure 6, respectively. In both cases bimodal ASEC chromatograms are observed with a very broad high molecular weight peak and a well-defined lower molecular weight peak corresponding to the unconverted macro-CTA.

To confirm that we had, in fact, employed functional macro-CTAs, self-blocking experiments were performed with each macro-CTA, resulting in near-quantitative blocking (DMA: M_n = 18 300, M_w/M_n = 1.09; VBTAC: M_n = 31 100, M_w/M_n = 1.14; Figure 6a,b). The poor blocking can therefore be attributed to the poor fragmentation of the macro-CTAs relative to the growing poly(DMAPMA) (**3** to **5** vs **3** to **4**, Scheme 3) and/or poor reinitiation by the poly(DMA) and poly(VBTAC) macroradicals (**5** to **7**, Scheme 3).[19] Indeed, the results are very similar to those reported earlier employing a poorly fragmenting/reinitiating low molecular weight CTA in the polymerization of styrenesulfonate.[8] Essentially, the presence of the α-methyl group in poly(DMAPMA) greatly weakens the C−S bond of the intermediate radical (**3**) such that fragmentation occurs preferentially toward the growing poly(DMAPMA) chain (**4**). Alternatively, slow reinitiation by the macroradical (**5**) would result in addition back to the dithioester before a DMAPMA monomer could add, thereby forestalling block copolymer formation.

Slow conversion of the macro-CTA to block copolymer has two primary effects on the polymerization. The first is that the number of block copolymer chains is much lower than the number of macro-CTAs in the reaction medium. To better describe this situation, eq 2 should be modified by replacing the initial concentration of CTA, $[CTA]_0$, with only the portion that has actually been converted to block copolymer, $[CTA]_{converted}$, yielding eq 3. It is readily apparent from comparison of eqs 2 and 3 that when $[CTA]_{converted} \ll [CTA]_0$, $M_{n,th}^* \gg M_{n,th}$.

$$M_{n,th}^* = \left(\frac{[M]_0 MW_{mon} p}{[CTA]_{converted}}\right) + MW_{CTA} \qquad (3)$$

The second major effect of slow conversion of the macro-CTA to block copolymer is a broadening of the polydispersity of the block copolymer. The preparation of polymers with narrow molecular weight distributions in a RAFT polymerization depends on the rapid conversion of CTA to macro-CTA (in the case of a homopolymerization) or macro-CTA to block copolymer (in the case of a block copolymerization).[64] Rapid conversion of the macro-CTA ensures that all of the second blocks are initiated at approximately the same time. Since the degenerative chain transfer mechanism ensures that all the chains are growing at approximately the same rate, block copolymers with narrow molecular weight distributions result. If the macro-CTA is converted very slowly to block copolymer, however, new block copolymer chains are started continuously at times between t = 0 and t_x. Block copolymers initiated early in the copolymerization grow to high molecular weight by t_x while those that are initiated at t_x have molecular weights very similar to the macro-CTA. The very broad molecular weight distributions observed in both block copolymerizations where DMAPMA was the second block are consistent with slow conversion of the macro-CTA to block copolymer (Figure 6).

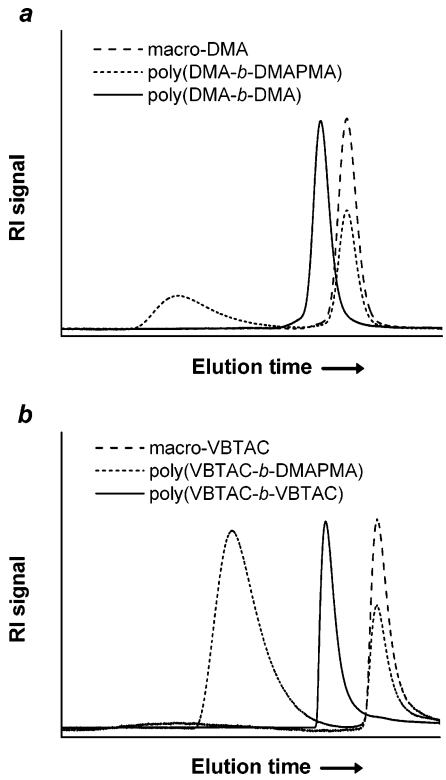


Figure 6. (a) ASEC traces of macro-DMA (M_n = 12 200, M_w/M_n = 1.12), the product of our unsuccessful attempt to prepare poly(DMA-*b*-DMAPMA) and successful poly(DMA-*b*-DMA) (M_n = 21 500, M_w/M_n = 1.06) obtained in an acetic acid/sodium acetate buffer, pH = 5, at 80 °C. (b) ASEC traces of macro-VBTAC (M_n = 5800, M_w/M_n = 1.08) and the products from our unsuccessful attempt to prepare poly(VBTAC-*b*-DMAPMA) and successful poly(VBTAC-*b*-VBTAC) (M_n = 31 100, M_w/M_n = 1.14) obtained in an acetic acid/sodium acetate buffer, pH = 5, at 70 °C.

Block copolymerizations employing macro-DMAPMA yield qualitatively different results (Figure 7a,b). As evidenced by comparison of the ASEC traces for the poly(DMAPMA-*b*-DMA) (M_n = 37 200, M_w/M_n = 1.14) and poly(DMAPMA-*b*-VBTAC) (M_n = 24 600, M_w/M_n = 1.11), starting with macro-DMAPMA allows controlled block copolymer formation. A small but observable amount of tailing suggests the presence of a limited quantity of dead macro-CTA; this was also observed in the self-blocking experiment.

Again, the α-methyl group decreases the strength of C−S bond, promoting the scission of the methacrylamido macroradical (**4**). The polymethacrylamido block is a better leaving group than either poly(DMA) or poly(VBTAC) (**3** to **4** vs **3** to **5**, Scheme 3). In the case where the poly(DMAPMA) block is formed first, however, the increased efficiency of fragmentation combined with efficient reinitiation results in rapid conversion of the macro-CTA to block copolymer. This is consistent with previously observed results in the copolymerization of styrene with methyl methacrylate in which the poor fragmentation/reinitiation efficiency of the polystyrene macroradical relative to the methyl methacrylate macroradical necessitated the synthesis of the poly(methyl methacrylate) block first.[19]

The compositions of the successfully synthesized block copolymers, poly(DMAPMA-*b*-VBTAC) and poly(DMAPMA-*b*-DMA), were determined by proton and carbon NMR spectroscopy, respectively. The ^{1}H NMR spectra of macro-DMAPMA (a), macro-VBTAC (b), and

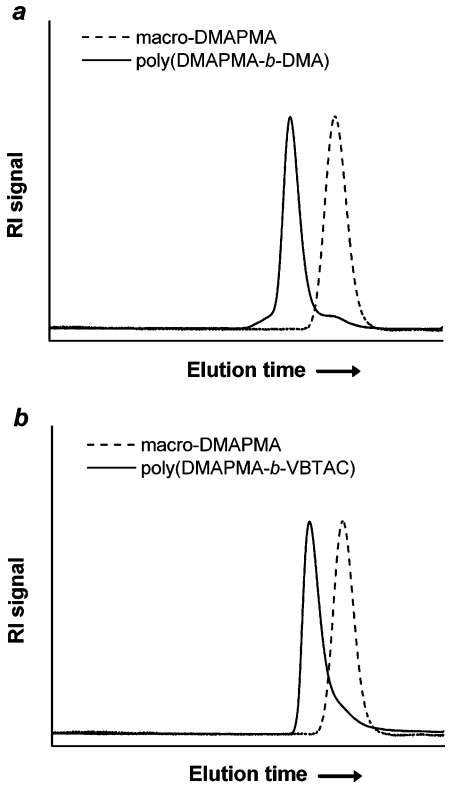


Figure 7. Successful block copolymerization employing macro-DMAPMA (M_n = 8700, M_w/M_n = 1.08) as the chain transfer agent: (a) poly(DMAPMA-*b*-DMA) (M_n = 37 200, M_w/M_n = 1.14) and (b) poly(DMAPMA-*b*-VBTAC) (M_n = 24 600, M_w/M_n = 1.11) obtained in an acetic acid/sodium acetate buffer, pH = 5, at 70 °C.

poly(DMAPMA-*b*-VBTAC) (c) are presented in Figure 8. Integration of the relative intensities of the peaks at 5.91−7.33 ppm corresponding to the four aromatic protons of poly(VBTAC) (**i** and **j**) and at 2.39−3.41 ppm corresponding to the nine methyl protons of poly(VBTAC) (**g**) and the 12 protons of macro-DMAPMA (**c** and **d**) indicate a block copolymer composition of 32:68 mol % DMAPMA:VBTAC. The copolymer composition of poly(DMAPMA-*b*-DMA) was determined to be 23:77 mol % DMAPMA:DMA by integration of the relative intensities of carbonyl peaks in the ^{13}C NMR spectrum at 181.6 ppm (macro-DMAPMA) and 178.1 ppm (poly(DMA)). The experimental values are very close to the theoretically predicted composition of the copolymers based on the molecular weight of the macro-CTA and the conversion of monomer in the blocking experiment (36:64 for poly(DMAPMA-*b*-VBTAC) and 28:72 for poly(DMAPMA-*b*-DMA)).

Conclusions

In conclusion, for the first time to our knowledge, the RAFT technique has been utilized in water to polymerize a methacrylamido monomer bearing a tertiary amine group, DMAPMA. Polymerization of DMAPMA in an acetate buffer was found to be far superior to that in DI H_2O alone, resulting in low-polydispersity polymers even at high conversion. The higher polymerization rate at a low CTA to initiator ratio ([CTA]/[I] = 1.5/1) in the buffer thus allows the highest conversions of monomer while still producing a well-defined homopolymer (M_n = 38 000, M_w/M_n = 1.12). The retention of dithioester

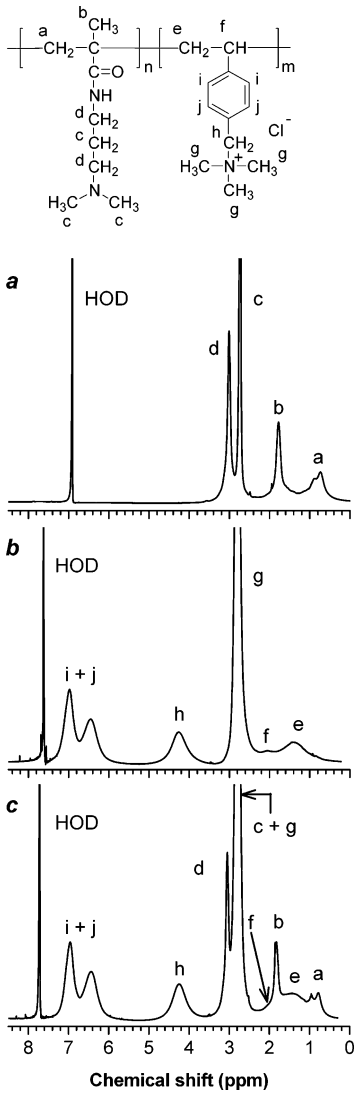


Figure 8. ^1H NMR spectra of (a) macro-DMAPMA, (b) macro-VBTAC, and (c) poly(DMAPMA-*b*-VBTAC) in 0.096 M NaCl D_2O solution containing 23.5 wt % DCl with DSS as an internal reference.

ends in the homopolymer was demonstrated by efficient chain extension of the macro-CTA. Purification conditions designed to limit CTA hydrolysis were found to be critical for successful retention of the chain ends. Blocking order was found to be important, with differences in fragmentation/reinitiation efficiency necessitating the synthesis of the DMAPMA block first. A DMAPMA macro-CTA was successfully employed in the block copolymerization of DMA and VBTAC, resulting in narrow polydispersity AB blocks (M_w/M_n = 1.14 and 1.11, respectively) with the compositions close to the theoretical ones. Studies of the stimuli responsive solution behavior of block copolymers of DMAPMA are currently under investigation in our lab and will be the subject of an upcoming report.

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