Water-Soluble Polymers. 84. Controlled Polymerization in Aqueous Media of Anionic Acrylamido Monomers via RAFT

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Polyacrylamide and its derivatives are an extremely important class of synthetic polymers used widely in industry.[1] To date, the synthesis of acrylamido-based homo- and copolymers has been achieved almost exclusively by conventional free radical polymerization methods.[2,3]

Considering economic and environmental issues, we have directed our efforts toward controlled free radical polymerization in aqueous media. We recently reported the synthesis, via RAFT, of homopolymers and block copolymers based on the water-soluble styrenic monomers, sodium 4-styrenesulfonate, sodium 4-styrenecarboxylate, *N*, *N*-dimethylvinylbenzylamine, and (*ar*-vinylbenzyl)trimethylammonium chloride.[4] Our group has a long-standing interest in acrylamido-based (co)polymers,[5] and this has prompted us to investigate the controlled radical polymerization of acrylamido monomers directly in aqueous media. Herein we report our initial RAFT polymerizations of two anionic acrylamido monomers: sodium 2-acrylamido-2-methylpropanesulfonate (AMPS) and sodium 3-acrylamido-3-methylbutanoate (AMBA) (Scheme 1). As far as we are aware, there are no prior reports regarding the attempted controlled polymerization of these two monomers in either organic or aqueous solution.

A review of the literature to date indicates that the controlled polymerization of acrylamido monomers by techniques such as nitroxide-mediated polymerization (NMP) or atom transfer radical polymerization (ATRP) is problematic, often requiring special conditions. Monomers are exclusively nonionic and polymerizations are conducted in organic solvents. Li and Brittain reported the polymerization of *N*,*N*-dimethylacrylamide (DMA) by NMP using TEMPO, but the process was not controlled.[6] With the development of more universal nitroxides, Benoit et al. subsequently demonstrated the ability to homo- and copolymerize DMA via NMP.[7] Molecular weights and polydispersity indices in the range 4000−48 000 and 1.10−1.21 were reported. Huang and Wirth reported the ATRP synthesis of polyacrylamide films grown on porous silica gel,[8] and Teodorescu and Matyjaszewski reported the ATRP of several different (meth)acrylamides.[9] However, Teodorescu and Matyjaszewski concluded that polymerization of (meth)acrylamide monomers via ATRP was not controlled. This was subsequently confirmed by Rademacher et al.[10] Senoo et al. have also reported the ATRP synthesis of PDMA employing the $RuCl_2(PPh_3)_3$-based initiating system, although resulting polydispersities were typically >1.60.[11] Recently, Rizzardo and coworkers reported a third pseudo-living polymerization technique they have termed reversible addition−fragmentation chain transfer polymerization (RAFT).[12] Significantly, the controlled polymerization of DMA[12e] and *N*-isopropylacrylamide[13] in organic media has already been demonstrated using this technique. Very few examples exist of controlled radical polymerization directly in aqueous media. Sodium 4-styrenesulfonate can be polymerized via nitroxide-mediated polymerization (NMP) in an ethylene glycol/water mixture,[14] and only recently has aqueous ATRP become a reality.[15]

Table 1. Conversion and Molecular Mass and Polydispersity Data for AMPS and AMBA Homopolymers and the Corresponding AMPS−AMBA and AMBA−AMPS Block Copolymers

sample	time (min)	conversion (%)	M_n (theory)	M_n (expt)[a]	M_w (expt)[a]	M_w/M_n[a]
AMPS1	255	77.1	26 500	24 400	31 500	1.29
AMPS2	343	88.0	17 600	19 500	22 600	1.16
AMPS3	8	>95.0[a]				
AMBA1	255	65.5	21 800	14 000	18 200	1.30
AMBA2	346	74.8	15 000	12 100	14 800	1.22
AMBA3	8	>95.0[a]				
PAMPS macro-CTA				33 900	38 600	1.14
P(AMPS-*b*-AMBA)			68 500	69 700	79 500	1.14
PAMBA macro-CTA				31 300	35 300	1.14
P(AMBA-*b*-AMPS)			64 400	57 900	67 200	1.16

[a] As determined by aqueous size exclusion chromatography, calibrated with poly(sodium 4-styrenesulfonate) standards in 20% MeCN/80% 0.1 M $NaNO_3$ eluent.

In the work reported here, anionic AMPS and AMBA homopolymers were synthesized in water by RAFT according to the procedure we previously reported [4,4′-azobis(4-cyanopentanoic acid) initiator, 4-cyanopentanoic acid dithiobenzoate as the RAFT chain transfer agent (CTA), 70 °C, H_2O], with the exception that the polymerizations were conducted under a nitrogen atmosphere, in round-bottomed flasks, equipped with a magnetic stir bar and sealed with a rubber septum as opposed to flame-sealed ampules (Scheme 1).[4] We also demonstrate the ability to synthesize AMPS−AMBA or AMBA−AMPS block copolymers in a controlled fashion, directly in aqueous media, employing PAMPS or PAMBA, respectively, as macro-CTAs. Homopolymer molecular masses were controlled by varying the monomer:CTA ratio. The initiator:CTA ratio was held constant at 1:5 (mole basis). The monomer concentration was 2.0 M. The solution pH was adjusted to ∼9.6 ± 0.2. (This was done primarily to ensure that AMBA was fully ionized.) Aliquots (0.74 mL) were removed from the polymerizations, via syringe, approximately every hour, diluted 100-fold with eluent, and then characterized by aqueous size exclusion chromatography (ASEC) (20% MeCN/80% 0.1 M $NaNO_3$ eluent, Viscotek TSK Viscogel column, Spectraphysics UV2000 detector, HP 1047A RI detector, poly(sodium 4-styrensulfonate) standards). The results for the synthesis of the AMPS and AMBA homopolymers are summarized in Table 1.

The CTA:monomer ratios were such that the theoretical M_n, at 100% conversion, for AMPS1 was 34 400 and 20 000 g/mol for AMPS2. Given that the molecular weights are reported as poly(sodium 4-styrenesulfonate) equivalents, the agreement between the theoretical and the observed values is good. The final observed polydispersity index (M_w/M_n), for AMPS2, of 1.16 is well

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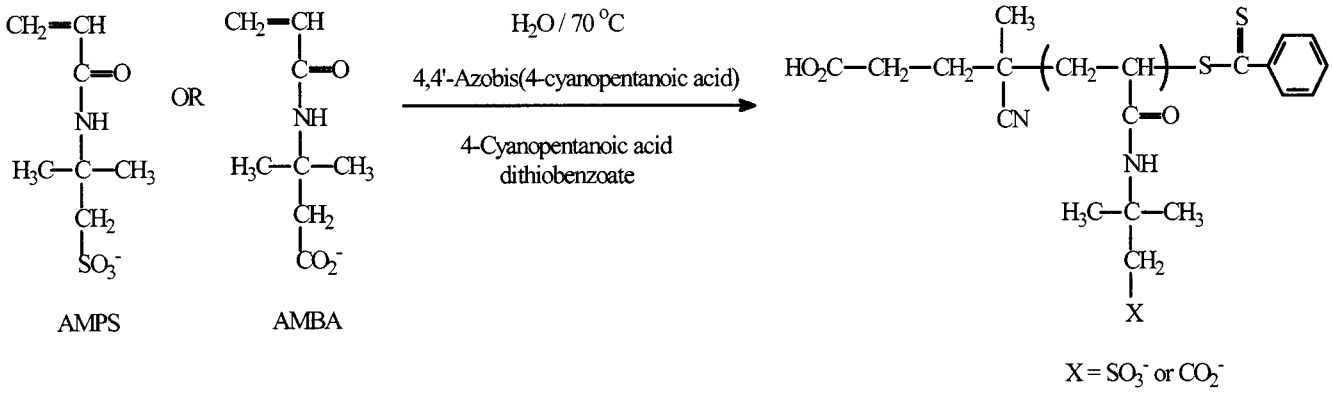
Scheme 1. Synthetic Outline for the Polymerization of AMPS and AMBA via RAFT



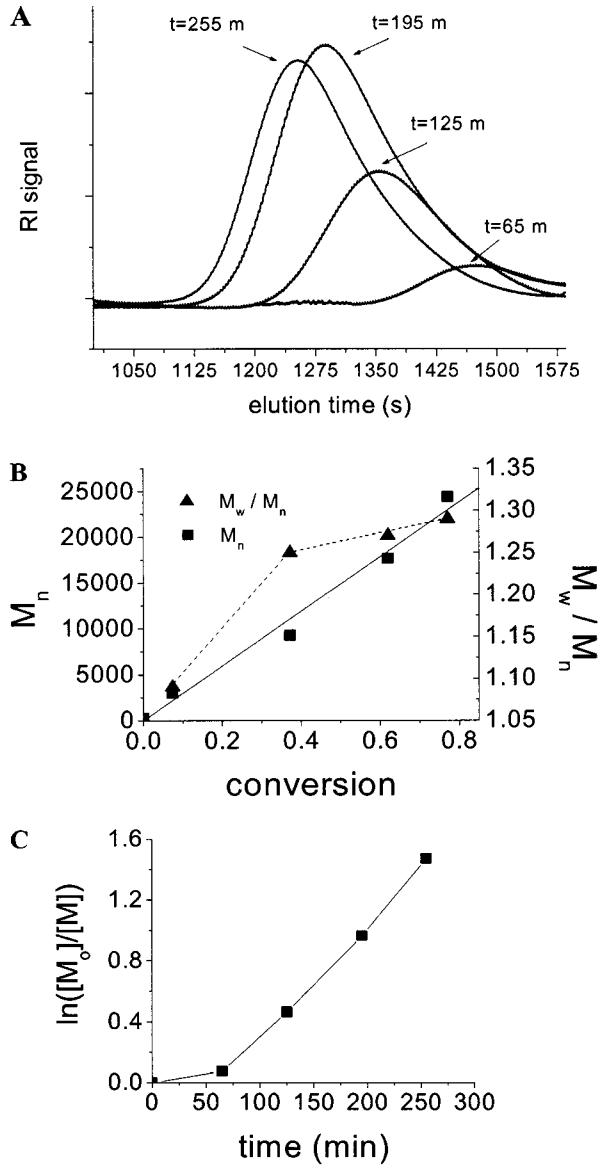


Figure 1. (A) ASEC chromatograms (RI traces) for AMPS1 showing the evolution of molecular mass with time and the plots of M_n vs conversion and M_w/M_n vs conversion (B) and the corresponding rate plot (C) for AMPS1.

below the theoretical lowest limit of 1.50 for a conventional free radical polymerization and can be considered to be near-monodisperse. The calculated polydispersity was slightly higher for AMPS1, at 1.29. Figure 1A shows an overlay of the RI traces from ASEC analysis for AMPS1 and clearly shows the observed increase in molecular mass with time.

Figure 1B shows the evolution of M_n and M_w/M_n with conversion for AMPS1, and Figure 1C shows the first-order rate plot. The conversion vs M_n plot is linear, indicating that the polymerization proceeded in a controlled fashion. The polydispersity increased with conversion showing a leveling trend above ca. 35% conversion but remained below 1.30. The first-order rate plot (Figure 1C) shows an induction period of approximately 1 h, after which the plot is linear, indicating the absence of termination reactions. We attribute the induction period to the slow initiation by the 4-cyanopentanoic acid radical fragment generated from the CTA.

A single AMPS homopolymer (AMPS3) was also synthesized by conventional free radical polymerization as a control. The experimental details were the same as the RAFT polymerizations except CTA was not added. In this instance, the reaction solution gelled within ~10 min. ASEC analysis indicated that the homopolymer was of high molecular weight, but the M_n could not be calculated since the sample eluted at the void volume of the column. AMBA homopolymers were synthesized under identical conditions as the AMPS homopolymers and similar results were obtained. As with the AMPS polymerizations, an induction period was observed using 4-cynaopentanoic acid dithiobenzoate as the RAFT CTA. Molecular weight control was good, and the polydispersities were narrow ($M_w/M_n \leq 1.30$). Likewise, a control polymerization in the absence of RAFT CTA yielded a high molecular weight homopolymer, which eluted at the void volume when analyzed by ASEC.

It is worth noting that we observe an increase in polydispersity with conversion (see Figure 1B). It has been generally shown that the polydispersity in "living" free radical polymerizations decreases with increasing conversion for ATRP and SFRP. Our observation is not unique for RAFT polymerizations and has been reported previously by Rizzardo et al. for several monomers including methyl acrylate, *N*-isopropylacrylamide, and vinyl acetate.[16]

PAMPS and PAMBA homopolymers were subsequently employed as macro-CTAs for the block copolymerization of the opposite monomer (i.e., RAFT-mediated PAMPS was used as the macro-CTA for the RAFT polymerization of AMBA, yielding a diblock copolymer of poly(AMPS-*block*-AMBA), and vice versa). Because of the high viscosities of the aqueous solutions of monomer and macro-CTA, the monomer concentration was reduced to 1.0 M for the block copolymeriza-

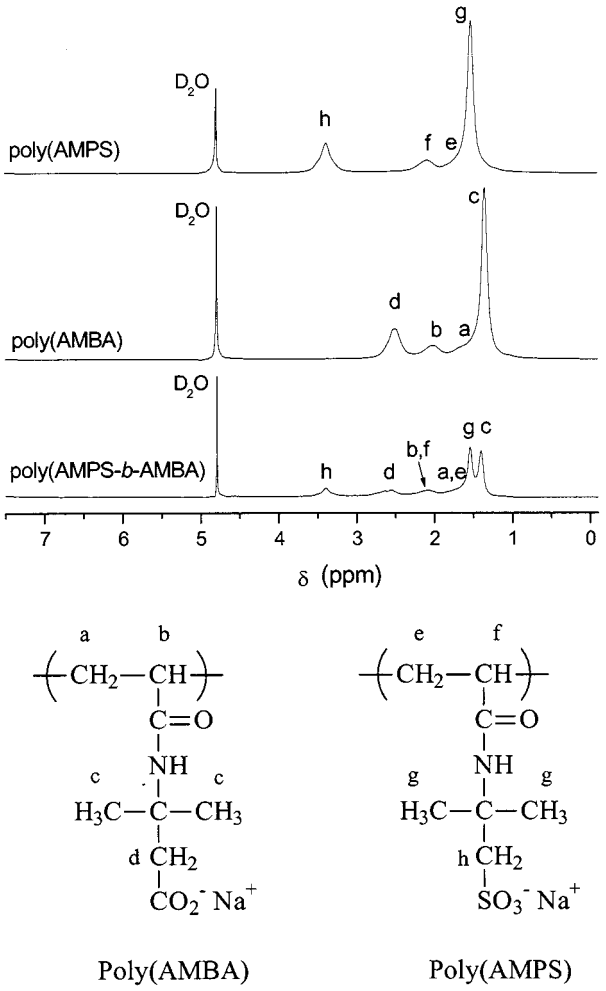


Figure 2. ^{1}H NMR spectra for the block copolymer of AMPS and AMBA along with the corresponding spectra for the homopolymers.

tions as opposed to the 2.0 M concentrations used in the preparation of the homopolymers. Given the lower monomer concentration, polymerization times were extended to approximately 13 h as compared to 6.5 h for the homopolymerizations. The ^{1}H NMR spectra with peak assignments for the homopolymers of AMPS and AMBA and the corresponding poly(AMPS-*block*-AMBA) copolymer are shown in Figure 2.

The copolymer is seen to be composed of monomeric units derived from both AMPS and AMBA. Integration of the peaks associated with the methylene protons (*d* and *h*) adjacent to the anionic functionalities yielded a copolymer composition of 46:54 (mol % basis) (AMPS:AMBA). This is in excellent agreement with the theoretical target composition of 45:55. Likewise, the block copolymer composition for the AMBA−AMPS diblock was found to be 49:51, with a target theoretical composition of 47:53.

Also listed in Table 1 is a summary of the molecular weights and polydispersities for the macro-CTAs and the corresponding block copolymers. Molecular weight distributions were determined using a Viscotek TRISEC detector, calibrated with poly(4-sodium styrenesulfonate) standards in the eluent described earlier. Data analysis was performed using software written in-house.

ASEC also provided confirmation of the diblock structure of the copolymers. The refractive index (RI) traces for the diblocks and the corresponding macro-CTAs are shown in Figure 3.

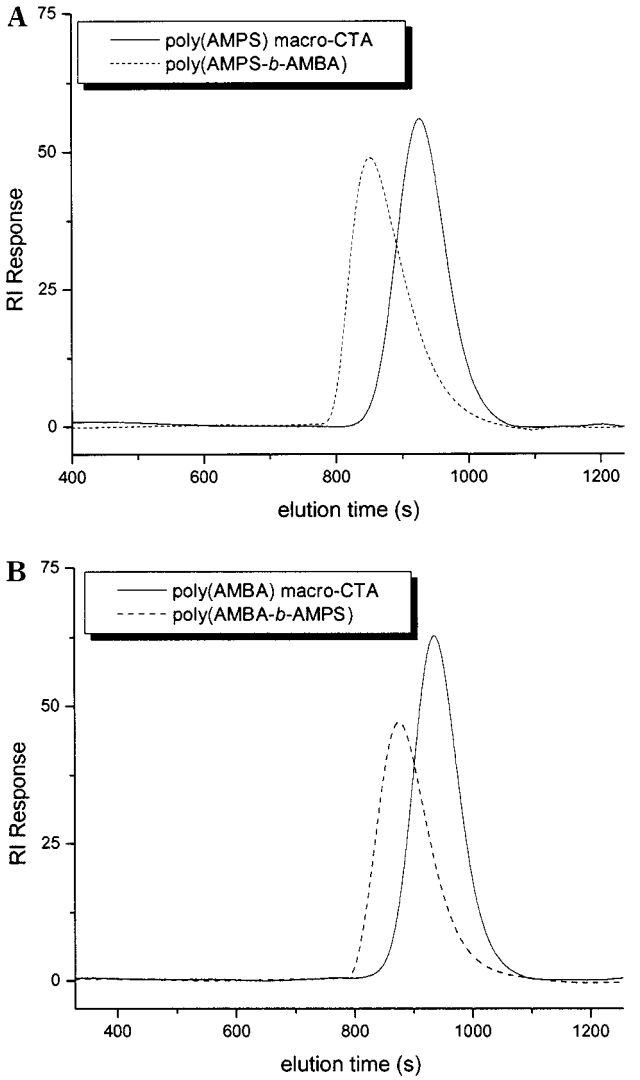


Figure 3. ASEC traces for the AMPS and AMBA macro-CTAs and the corresponding diblock copolymers.

The block copolymer derived from the PAMPS macro-CTA had a theoretical M_n of 68 500 while the experimental value was determined to be 69 700 with a corresponding PDI of 1.14. Again, there is excellent agreement between the theoretical and experimental values. Additionally, as evidenced by the molecular weight distributions, there appears to be no significant homopolymer impurity in the block copolymers implying that most of the chain ends of both the AMPS and AMBA homopolymers were functionalized with dithioester end groups and underwent subsequent addition with the corresponding comonomer.

Clearly the ability to polymerize these monomers in a controlled fashion in aqueous media via RAFT is highly beneficial and should facilitate the synthesis of more complex, hitherto unattainable, architectures.

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References and Notes

(1) Shalaby, S. W.; McCormick, C. L.; Butler, G. B. *Water-Soluble Polymers: Synthesis, Solution Properties and Ap-*

plications; ACS Symposium Series 467; American Chemical Society: Washington, DC, 1991.
(2) (a) Kathmann, E. E. L.; White, L. A.; McCormick, C. L. *Macromolecules* **1997**, *30*, 5297. (b) Kathmann, E. E. L.; McCormick, C. L. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 243.
(3) Koňák, Č.; Oupický, D.; Chytrý, V.; Ulbrich, K.; Helmstedt, M. *Macromolecules* **2000**, *33*, 5318.
(4) Mitsukami, Y.; Donovan, M. S.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2001**, *34*, 2248.
(5) (a) Kathmann, E. E.; White, L. A.; McCormick, C. L. *Polymer* **1997**, *34*, 871. (b) Kathmann, E. E.; McCormick, C. L. *J. Polym. Sci., Polym. Chem.* **1997**, *35*, 231. (c) Kathmann, E. E.; White, L. A.; McCormick, C. L. *Macromolecules* **1997**, *30*, 5297.
(6) Li, D.; Brittain, W. J. *Macromolecules* **1998**, *31*, 3852.
(7) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *J. Am. Chem. Soc.* **1999**, *121*, 3904.
(8) Huang, X.; Wirth, M. J. *Macromolecules* **1999**, *32*, 1694.
(9) Teodorescu, M.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 4826.
(10) Rademacher, J. T.; Baum, M.; Pallack, M. E.; Brittain, W. J.; Simonsick, W. J. *Macromolecules* **2000**, *33*, 284.
(11) Senoo, M.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 8005.
(12) (a) Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. WO Patent 9801478, 1998. (b) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Le, T. P.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559. (c) Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Thang, S. H. *Macromol. Symp.* **1999**, *143*, 291. (d) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071. (e) Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 2071.
(13) Ganachaud, F.; Monteiro, M. J.; Gilbert, R. G.; Dourges, M.-A.; Thang, S. H.; Rizzardo, E. *Macromolecules* **2000**, *33*, 6738.
(14) Keoshkerian, B.; Georges, M. K.; Boils-Bossier, D. *Macromolecules* **1995**, *28*, 6381.
(15) (a) Ashford, E. J.; Naldi, V.; O'Dell, R.; Billingham, N. C.; Armes, S. P. *Chem. Commun.* **1999**, 1285. (b) Wang, X.-S.; Lascelles, S. F.; Jackson, R. A.; Armes, S. P. *Chem. Commun.* **1999**, 1817. (c) Wang, X.-S.; Jackson, R. A.; Armes, S. P. *Macromolecules* **2000**, *33*, 255.
(16) Rizzardo, E.; Chiefari, J.; Mayadunne, R. T. A.; Moad, G.; Thang, S. H. *Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000; pp 278−296.

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