RAFT Polymerization of *N*,*N*-Dimethylacrylamide in Water†

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Introduction. Controlled radical polymerization[1] (CRP) has been the focus of intense research in recent years. Atom transfer radical polymerization (ATRP),[2] nitroxide-mediated polymerization (NMP),[3] and more recently, reversible addition−fragmentation chain transfer polymerization (RAFT)[4] have allowed for the synthesis of (co)polymers with designated molecular weights and narrow molecular weight distributions.

Considering the advantages of precisely controlled structures and the need for environmentally viable technologies, we have recently centered our efforts on conducting CRP in aqueous media. We first 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.[5] Subsequently, we reported the first example of CRP of anionic acrylamido monomers in aqueous media.[6]

As well as ionic monomers, we are interested in polymerizing nonionic hydrophilic/water-soluble species, such as *N*,*N*-dimethylacrylamide (DMA) via RAFT. Herein, we report the CRP of DMA, in aqueous media, utilizing two RAFT CTAs, Table 1. As far as we are aware, this constitutes the first report outlining the CRP of this monomer via RAFT in water.

The CRP of DMA, and acrylamido monomers in general, has proven to be challenging using techniques such as ATRP and NMP. Li and Brittain reported the polymerization of DMA by NMP using TEMPO, but the process was shown to be uncontrolled.[7] However, with the development of more universal nitroxides, Benoit et al. demonstrated the ability to (co)polymerize DMA via NMP.[8] Teodorescu and Matyjaszewski reported the ATRP of several (meth)acrylamides.[9] However, the authors concluded that these systems were not "living". This was subsequently confirmed by Rademacher et al.[10] Senoo et al. reported the ATRP synthesis of PDMA, employing the $RuCl_2(PPh_3)_3$-based initiating system, although resulting polydispersities were typically >1.60.[11] With the discovery of RAFT, a wider range of monomers are now amenable to CRP. Significantly, the CRP of DMA[12] and *N*-isopropylacrylamide,[13] via RAFT, in *organic* media have already been demonstrated.

In the work reported here, DMA homopolymers were synthesized in water via RAFT. Both sodium 4-cyanopentanoic acid dithiobenzoate (CTPNa) and *N*,*N*-dimethyl-s-thiobenzoylthiopropionamide (TBP) were employed as the RAFT chain transfer agents (CTAs). CTPNa was chosen due to its inherent water-solubility and its ability to mediate the controlled polymerization of anionic acrylamido monomers in aqueous media,[6] while TBP was selected since we have recently demonstrated the effectiveness of this CTA for the polymerization of DMA in organic media.[12a] 4,4′-Azobis(4-cyanopentanoic acid) (V-501) was utilized as the free radical initiator with a CTA/I ratio of 5/1, [DMA] = 1.83 M, [V-501] = 9.2×10^{-4} M, and [CTA] = 4.57×10^{-3} M. The CTA/monomer ratios were chosen for a theoretical M_n of 40 000 at 100% converison. The solutions were purged for 30 min with nitrogen to remove oxygen. The solutions were transferred, via cannula, to rubber-septa-sealed test tubes which were prepurged with nitrogen. These were immersed in a water-bath at three temperatures: 60, 70, and 80 °C. The samples were removed after various time intervals (up to 9.5 h), cooled in ice water, and stored in a freezer.

The samples were analyzed by NMR spectroscopy (using a water-suppression technique) to determine conversion. A portion of each sample was diluted and analyzed by aqueous size exclusion chromatography (ASEC) (using an eluent of 20% acetonitrile/80% 0.05 M Na_2SO_4, a Viscotek TSK Viscogel 4000PWxL column, and Polymer Labs LC 1200 UV/vis, Wyatt Optilab DSP Interferometric refractometer, and Wyatt DAWN EOS multiangle laser light scattering detectors). The d*n*/d*c* of PDMA in the above eluent was determined to be 0.1645 at 25 °C. The molecular weight and polydispersity data were determined using the Wyatt ASTRA SEC/LS software package.

Results and Discussion. Figure 1 shows an example of the evolution of molecular weight, as determined by ASEC, on direct aliquots from the PDMA homopolymer synthesized using CTPNa at 80 °C. An increase in the molecular weight (peak shifts to shorter retention times) is observed which is, at least qualitatively, indicative of a controlled polymerization.[1] There is evidence in the chromatograms, at $T \geq 160$ min, of a small amount of high molecular weight species arising from uncontrolled polymerization or termination events (high molecular weight shoulder). This is not observed in chromatograms of the TBP-mediated polymerization at the same temperature (see insert).

The kinetic plots for the CTPNa- and TBP-mediated polymerizations of DMA utilizing the 5/1 ratio of CTA/I are shown in Figure 2. Several features are to be noted. The CTPNa-mediated polymerizations (solid symbols) show the expected increases in rate with increasing temperature. Successful polymerization in the presence of TBP (open triangle) in water occurred only at 80 °C with much lower rates of monomer consumption at 60 and 70 °C (data not shown). Comparison of the plots with CTPNa (solid triangle) and TBP at 80 °C also reveals an early retardation with the latter, eventually followed by a rate of polymerization similar to that observed with CTPNa.

The differences in kinetic behavior between TBP and CTPNa are likely a reflection of the relative fragmentation efficiencies (ability of the growing polymer radicals to react with CTA and subsequently expel the respective R groups) in water. Factors including leaving group stability and hydrophobicity affect when the RAFT preequilibrium is completed and the main RAFT equilibrium is established. The addition of increasing

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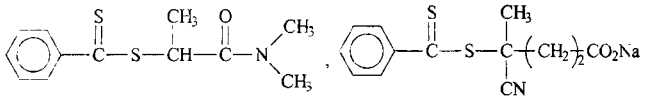
Table 1. Molecular Weight (Theoretical and Experimental), Polydispersity, and Conversion Data for PDMAs Synthesized in Aqueous Media in the Presence of TBP and CTPNa

CTA[a]	temp (°C)	time (min)	convn (%)[b]	M_n(theory)[c]	M_n(expt)[d]	M_w/M_n[d]
TBP	60	580	1	400	7400	1.67
TBP	70	580	25	10 000	30 600	1.17
TBP	80	160	66	26 400	43 500	1.14
TBP (0.9 M DMF)	80	160	66	26 400	39 300	1.14
TBP (1.8 M DMF)	80	160	68	27 200	34 700	1.23
TBP (3.6 M DMF)	80	160	69	27 600	34 400	1.20
CTPNa	60	160	48	19 200	25 560	1.11
CTPNa	70	160	80	32 000	41 130	1.15
CTPNa	80	160	87	34 800	45 570	1.14

[a] Structures of TBP and CTPNa respectively:



[b] As determined by NMR spectroscopy. [c] M_n(theory) = {([M] × MW_{mon})/[CTA]) × % conversion} + MW_{CTA}.[3] [d] As determined by ASEC in 20% MeCN/80% 0.05 M Na_2SO_4 employing RI and light scattering detectors.

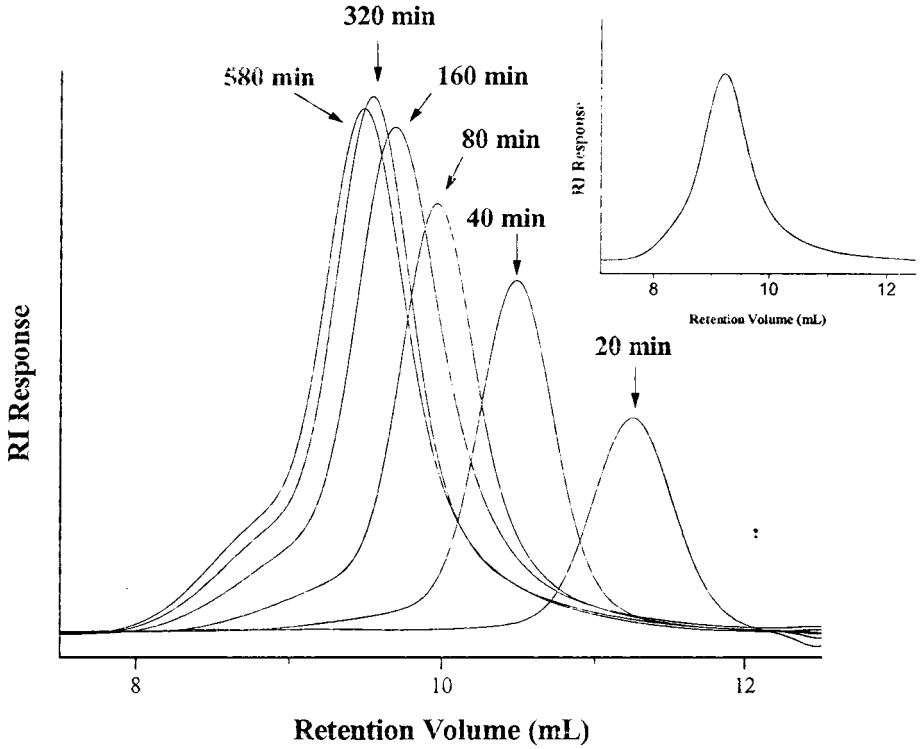


Figure 1. Aqueous size exclusion chromatograms for PDMA synthesized in the presence of CTPNa in water at 80 °C. The insert shows PDMA synthesized under identical conditions in the presence of TBP.

amounts of *N*,*N*-dimethylformamide (DMF) (as demonstrated in Figure 2) diminishes the initial retardation observed with TBP.

The molecular weight vs conversion data for the CTPNa- and TBP-mediated polymerizations of DMA are shown in Figure 3. The plots in water alone for TBP at 80 °C and CTPNa at 60, 70, and 80 °C, respectively, are linear and exhibit identical slopes, though the former has a nonzero intercept. Addition of sufficient quantities of DMF to the TBP-mediated polymerizations, at 80 °C, results in a remarkably linear relationship between experimentally determined molecular weight and conversion. This can be compared to the theoretical projection of molecular weight vs conversion (dotted line in Figure 3) of an ideal RAFT polymerization.[12b]

The data presented in Figures 1−3 and Table 1 appear to be at least qualitatively consistent with the kinetic scheme described previously by Rizzardo et al.[12b] and modeled by Davis et al.[14] for RAFT polymerizations. The main RAFT equilibrium should be reached rapidly with efficient addition/fragmentation of RAFT agent and reinitiation in the preequilibrium steps. It appears that at temperatures of 60 and 70 °C, TBP does not fragment efficiently in water, preventing controlled chain growth (Table 1). At 80 °C in water, the main equilibrium is eventually reached; however during the early stages, noncontrolled initiator-induced polymerization occurs. Controlled chain growth is realized at all three temperatures with CTPNa and at 80 °C with TBP. Molecular weights are somewhat higher than theoretically predicted, possibly due to early "non-RAFT" propagation and/or radical coupling inherent to CRP processes. An additional consideration is the low but finite, temperature-dependent CTA and macroCTA hydrolysis expected during aqueous polymerization.[15] Addition of DMF to aqueous solutions of TBP-mediated polymerizations results in better molecular weight control (Table

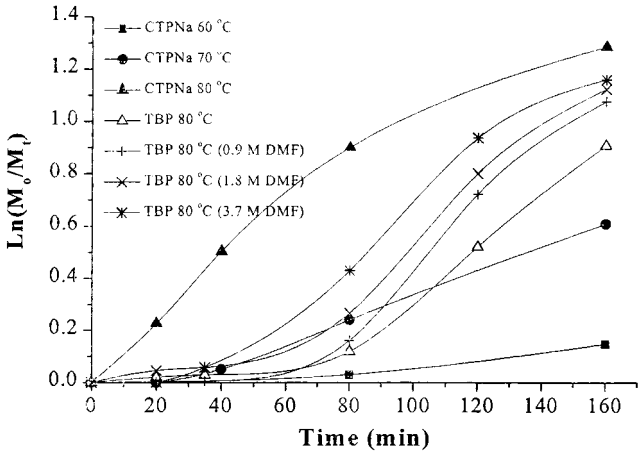


Figure 2. Kinetic plots for the polymerization of DMA in the presence of CTPNa at 60 (■), 70 (●), and 80 °C (▲) and in the presence of TBP at 80 °C for concentrations of 0.0 (△), 0.9 (+), 1.8 (×), and 3.7 M (∗) DMF/H_2O.

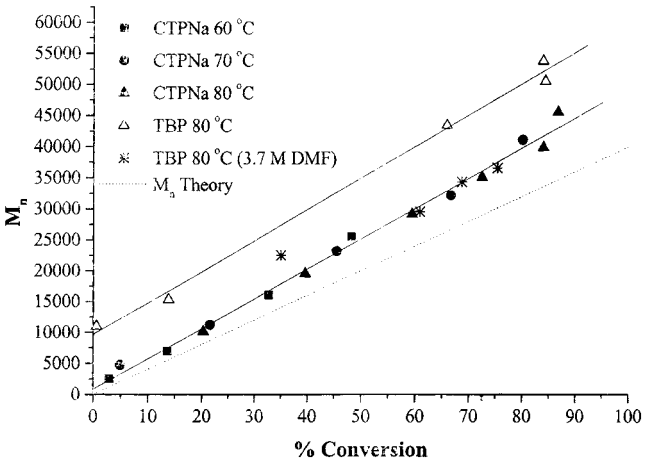


Figure 3. Plots of molecular weight vs conversion for PDMA synthesized at 60 (■), 70 (●), and 80 °C (▲) in the presence of CTPNa, at 80 °C in the presence of TBP (△), and at 80 °C in 3.7 M DMF/H_2O in the presence of TBP (∗).

1). It is also clear from Table 1 that M_w/M_n values ranging from 1.11 to 1.23 are well within the limits for controlled polymerizations.

Recently, we have reported an extensive study of the RAFT polymerization of DMA utilizing TBP and other CTAs in benzene.[12a] In those studies TBP was especially effective for mediating DMA polymerization at 60 °C, proceeding in a facile manner with no observable retardation. That the DMA polymerizations with this CTA in water did not proceed in a controlled manner at 60 or 70 °C is somewhat surprising given that fragmentation and reinitiation, according to the current kinetic models, should be quite favorable in this highly polar solvent. Although not the focus of this communication, studies are underway in our laboratories to further elucidate the role of CTA structure in the process of RAFT polymerization in water.

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(15) Preliminary experiments indicate that both TBP and CTPNa are susceptible to some hydrolysis at the temperatures of this study, with TBP being more readily hydrolyzed—this may account for the discrepancies between the observed and theoretical molecular weights. The results form these experiments will be reported in an upcoming paper: Donovan, M. S.; Lowe, A. B.; Sumerlin, B. S.; McCormick, C. L. Manuscript in preparation.

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