Atom Transfer Radical Polymerization of *N*,*N*-Dimethylacrylamide

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ABSTRACT: The polymerization of *N*,*N*-dimethylacrylamide (DMA) under atom transfer radical polymerization (ATRP) conditions was studied. The ligand, solvent (water, *n*-butanol, and toluene), initiator, and Cu halide were varied. High monomer conversions were obtained using the Me_4Cyclam ligand. Polymerizations in water that were initiated at room temperature were complete within minutes. However, none of the experimental conditions produced a controlled polymerization. This conclusion is based on broad molecular weight distributions, poor agreement between theoretical and experimental M_n, incremental monomer addition experiments, and end group analysis. We believe that the Cu salts complex to the amide group of the chain ends and stabilize the radical. This stabilization retards the deactivation step in ATRP and produces an unacceptably high concentration of radicals which leads to spontaneous termination reactions. In addition, we have indirect evidence for a cyclization reaction involving nucleophilic Br displacement by the penultimate amide nitrogen; this cyclic onium intermediate undergoes hydrolysis to form a hydroxy-terminated polymer.

Introduction

Research in living free radical polymerization[1] has become an active area of polymer synthesis. Work has been published on nitroxide-mediated processes,[2,3] atom transfer radical polymerization (ATRP),[1] and radical addition and fragmentation technique (RAFT).[4] Most work on living radical polymerization has focused on styrene and (meth)acrylates. Our particular interest in living radical polymerization has concentrated on the polymerization of acrylamide-base monomers.[5] Polyacrylamides are an important class of water-soluble polymers,[6] and methods for controlled polymerization would be very valuable. Xie and Hogen-Esch[7] have described the anionic polymerization of acrylamide monomers; these workers produced polyacrylamides with controlled molecular weight and narrow molecular weight distributions when polymerizations were conducted at low temperatures (−78 °C).

The living free radical polymerization of acrylamides has not been widely studied. Recent reports have demonstrated controlled polymerizations using the nitroxide-mediated process[2] and RAFT.[4] Therefore, these successful living polymerizations confirm that, compared to styrene- and acrylate-based monomers, there is nothing intrinsically difficult about conducting living radical polymerizations of acrylamides. After considerable experimental effort, we have concluded that ATRP is not an appropriate method for the living radical polymerizations of acrylamides. A similar conclusion was reached by Teodorescu and Matyjaszewski[8] in a recent report on ATRP of (meth)acrylamides that appeared in print just prior to completion of this paper. In this report, we will detail our results, compare our study to the work of Matyjaszewski, offer an explanation for the failure of ATRP of acrylamides, and comment on literature reports that claim living polymerization of acrylamides via ATRP.[9]

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Experimental Section

Materials. Dichloromethane, triethylamine, dimethylamine hydrochloride, ethyl 2-bromoisobutyrate, 2-bromopropionyl bromide, 2-chloropropionyl chloride, and aluminum oxide (basic) were all used as received from Aldrich. *N*,*N*-Dimethylacrylamide (DMA, Aldrich) was purified by vacuum distillation to remove stabilizer. *Ligands:* Tris[2-(dimethylamino)ethyl]-amine (Me_6-TREN) was synthesized as described in the literature.[10] 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam, Acros) was used as received. 1,1,4,7,10,10-Hexamethyltriethylenetetraamine (HMTETA) (Aldrich) was used as received. *Copper halides:* CuBr (Aldrich) was purified as described in the literature.[11] CuCl (99.995%, Aldrich) was used as received. *Solvents:* toluene (Aldrich, anhydrous grade) and *N*,*N*-dimethylformamide (DMF, Aldrich, anhydrous grade) were used as received. Water was purified by the Millipore Milli-Q system.

Synthesis of *N*,*N*-Dimethyl-2-bromopropionamide (2). A 500 mL round-bottom flask containing 150 mL of CH_2Cl_2 was cooled in an ice bath, and Et_3N (25 mL, 0.180 mol) and Me_2NH_2Cl (9.4 g, 0.115 mol) were added. After 20 min, 2-bromopropionyl bromide (10 mL, 0.095 mol) was added dropwise over a period of 10 min. The reaction was stirred at 0 °C for 30 min and then at room temperature for 2 h. A 50 mL aliquot of water and 2 mL of Et_3N were added. The organic layer was washed with 50 mL of 5% $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated in vacuo to afford a yellow oil. Vacuum distillation at 70 °C (1 mmHg) gave 13.43 g (78%) of a clear liquid. ^{1}H NMR ($CDCl_3$): δ 1.8 (d, 3H, −CHCH_3), 3.0 (d, 6H, −N(CH_3)$_2$), 4.5 (q, 1H, −CH).

The same procedure was used to synthesize *N*,*N*-dimethyl-2-chloropropionamide (**3**). Vacuum distillation gave 75% yield.

General Polymerizations. A single-neck round-bottom flask equipped with a stir bar was charged with DMA (100 equiv), DMF (0.1 mL per 1 mL of monomer), solvent (0.9 mL per 1 mL of monomer), and ligand (1 equiv). After degassing with argon for 20 min, CuX (1 equiv) was added. The solution was degassed for an additional 10 min, and initiator (1 equiv) was added via syringe. The reaction was carried out at the specified temperature using a preheated oil bath if necessary. The mixture was reacted to high conversion, which was monitored by ^{1}H NMR. For characterization, the sample was dissolved in acetone and filtered through a basic alumina plug

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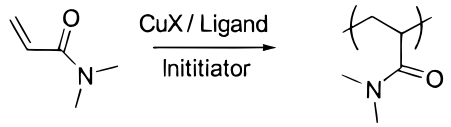
Scheme 1



to remove catalyst. Solvent was removed and sample was analyzed by GPC and electrospray mass spectrometry (MS).

Incremental Monomer Addition Polymerizations. A single-neck round-bottom flask equipped with a stir bar was charged with DMA (25 equiv), DMF (0.4 mL per 1 mL of monomer), toluene (3.6 mL per 1 mL of monomer), and Me_4-Cyclam (1 equiv). After degassing with argon for 20 min, CuBr (1 equiv) was added. The solution was degassed for an additional 10 min, and ethyl 2-bromoisobutyrate (1 equiv) was added via syringe. The mixture was reacted for 1 h. The second monomer increment (25 equiv), CuBr (1 equiv), and Me_4-Cyclam (1 equiv) were added, and the reaction was stirred for 2 h. For characterization, the sample was dissolved in acetone and filtered through a basic alumina plug to remove catalyst. Solvent was removed and sample was analyzed by GPC.

Characterization. ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer. Routine molecular weight analysis was performed with a Waters 515 pump, 2 PLgel (Polymer Laboratories) mixed D columns (5 μ), and a Waters 410 differential refractometer. The eluent was DMF, and the flow rate was 0.7 mL/min. Molecular weights were calibrated by comparison to narrow MWD samples of PMMA standards (Polymer Laboratories). Data analysis was performed with the Scientific Software, Inc., E-Z Chrom software package. The electrospray data were collected on the Finnigan FTMS 2001 equipped with an Ultrasource I interface. The details of sample preparation and the parameters for electrospray ionization are published.[12]

Results

For our work, we chose *N,N*-dimethylacrylamide (DMA) as the monomer and used monomer/initiator ratios such that theoretical M_n = 10 000 g/mol (see Scheme 1). Teodorescu and Matyjaszewki[8] explored a greater variety of (meth)acrylamide structures but concentrated on polymerizations in bulk and methanol as a solvent. In an attempt to successfully achieve ATRP of DMA, we explored the effect of initiator structure, solvent, ligand, and halogen. For all experiments, we used monomer conversion, experimental M_n, and M_w/M_n as measures of success. In selected cases, we also tried resumptive experiments where a second aliquot of monomer was added. We observed a blue precipitate during polymerizations in toluene/DMF, a small amount of precipitate in alcohol solvents, and no precipitate in aqueous polymerizations. For all experiments, we employed experimental techniques that eliminated the effect of oxygen on the outcome of the reactions.

It is important to note that our molecular weights are based on GPC measurements in which molecular weights were calibrated against PMMA standards. Therefore, when considering results from GPC, we have tried to concentrate on trends rather than individual measurements. For selected low molecular weight samples, we were able to assess M_n via ^{1}H NMR or MS. For room-temperature experiments, no attempt was made to control the exotherm (if any) so that the actual, average polymerization temperature may be higher than 25 °C.

Initiator. A common ATRP initiator for (meth)-acrylates is ethyl 2-bromoisobutyrate (**1**). Because we anticipated performing polymerizations in a variety of solvents, we synthesized water-soluble initiators, 2-bromopropanamide (**2**) and 2-chloropropanamide (**3**). Initiators **1** and **2** behave similarly; see Table 1. Both initiators give nearly complete monomer conversions in 1 h or less at room temperature. The polymers were characterized by a broad polydispersity and poor agreement between theoretical and experimental M_n.

Table 1. ATRP of DMA Using Initiators 1 and 2[a]

initiator	% conversion	exp M_n, g/mol[b]	M_w/M_n
1	90	29 000	1.7
2	98	36 000	2.1

[a] ATRP conditions: [DMA] = 4.8 M; [CuBr] = 0.048 M; [**6**] = 0.048 M; [initiator] = 0.048 M; solvent = toluene/DMF, 9:1 (v/v); room temperature, 1 h; M_n(theoretical) = 10 000 g/mol. [b] M_n obtained by GPC.

Table 2. ATRP of DMA Using Different Solvent Systems[a]

solvent system	% conversion	exp M_n, g/mol[c]	M_w/M_n
toluene/DMF (9:1)	98	36 000	2.1
H_2O/DMF (9:1)	90	48 000	2.2
butanol/DMF (9:1)	75	22 000	2.6
bulk[b]	90	43 000	1.6

[a] ATRP conditions: [DMA] = 4.8 M; [CuBr] = 0.048 M; [**6**] = 0.048 M; [**1**] = 0.048 M; room temperature, 1 h; M_n(theoretical) = 10 000 g/mol. [b] Reaction time <1 min. [c] M_n obtained by GPC.

Table 3. ATRP of DMA Using Ligands 4, 5, and 6 in DMF[a]

ligand	% conversion	exp M_n, g/mol[d]	M_w/M_n
4	trace	10 000	2.5
5[b]	20	900	
6[c]	95	33 000	2.2

[a] ATRP conditions: [DMA] = 4.8 M; [CuBr] = 0.048 M; [ligand] = 0.048 M; [**2**] = 0.048 M; solvent = DMF; 90 °C, 6 h; M_n(theoretical) = 10 000 g/mol. [b] Low MW of polymer led to interference with solvent peaks in GPC and made it difficult to determine PDI. [c] Reaction time = 1 h, room temperature. [d] M_n obtained by GPC.

Solvent. Different polymerization solvent systems were investigated, and their results were compared to polymerizations in bulk. DMF was used as a ^{1}H NMR standard to determine conversion. Both toluene and H_2O gave similar results, where *n*-butanol led to low monomer conversion; see Table 2. When water was investigated as a potential solvent for the polymerization of DMA, very fast reaction rates (<1 min for 100% conversion) were observed. Overall, solution polymerizations gave products characterized by broader polydispersities than bulk reactions. However, reaction times for bulk polymerizations were faster than those for the solution polymerizations. Again, poor agreements between theoretical and experimental M_n were observed in all cases.

Ligand. A commonly used ATRP ligand for acrylate polymerizations is HMTETA (**4**). In polymerizations of DMA, more strongly complexing ligands such as Me_6-TREN (**5**) and Me_4Cyclam (**6**) were used. Polymerization reaction rates increased in the order **4** < **5** < **6**, and broad polydispersities were observed; see Tables 3−5. Poor agreements between theoretical and experimental M_n were again observed.

Halogen. The behavior of brominated systems (CuBr/**2**) and chlorinated systems (CuCl/**3**) was studied and compared. The chlorinated systems led to much slower reaction rates and lower conversions as seen previously;[13] see Table 6. When using **2** and varying the halide salt, no difference was observed between reactions. The choice of halogen did not have a significant effect on polydispersity.

Scheme 2

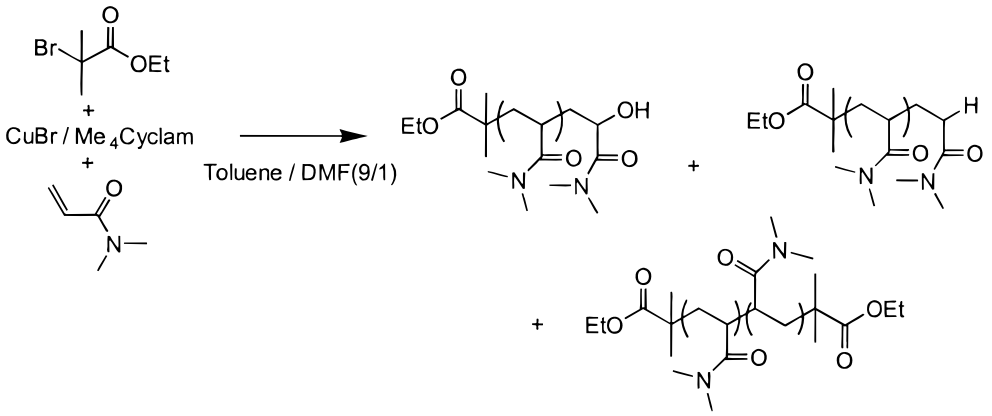


Table 4. ATRP of DMA Using Ligands 4, 5, and 6 in Water[a]

ligand	% conversion	exp M_n, g/mol[c]	M_w/M_n
4[b]	30	45 000	4.2
5	45	25 000	5.2
6	90	48 000	2.2

[a] ATRP conditions: [DMA] = 4.8 M; [CuBr] = 0.048 M; [ligand] = 0.048 M; [**2**] = 0.048 M; solvent = H_2O/DMF, 9:1 (v/v); room temperature, 1 h; M_n(theoretical) = 10 000 g/mol. [b] Solvent = H_2O/DMF, 5:5 (v/v); reaction time = 6 h, 90 °C. [c] M_n obtained by GPC.

Table 5. ATRP of Bulk DMA Using Ligands 5 and 6[a]

ligand	% conversion	exp M_n, g/mol[d]	M_w/M_n
5	89	7 000	1.4
6[b]	90[c]	43 000	1.6

[a] ATRP conditions: [DMA] = 9.7 M (bulk); [CuBr] = 0.097 M; [ligand] = 0.097 M; [**2**] = 0.097 M; room temperature, 3 h; M_n(theoretical) = 10 000 g/mol. [b] Reaction time <1 min. [c] Excessive gelling of reaction made determination of conversion difficult. [d] M_n obtained by GPC.

Table 6. ATRP of DMA Using Different Halogen Systems in Solution[a]

halogen system	% conversion	exp M_n, g/mol[c]	M_w/M_n
CuBr/**2**	98	36 000	2.1
CuCl/**3**[b]	35	47 000	2.2
CuI/**2**	98	21 000	2.1

[a] ATRP conditions: [DMA] = 4.8 M; [CuX] = 0.048 M, [**6**] = 0.048 M; [initiator] = 0.048 M; solvent = toluene/DMF, 9:1 (v/v); room temperature, 1 h; M_n(theoretical) = 10 000 g/mol. [b] Reaction time = 24 h. [c] M_n obtained by GPC.

Resumption Experiment. The incremental monomer addition polymerization experiment was performed in 9:1 toluene:DMF (Scheme 2).

The target M_n for the first monomer addition was 2500 g/mol. The addition of the first fraction of monomer resulted in 96% conversion; M_n(GPC) = 9900 g/mol, M_n(^{1}H NMR) = 3000 g/mol, and PDI = 1.5. After 1 h reaction time, the second increment of monomer was added (theoretical M_n = 5000 g/mol); we found it necessary to add monomer, CuX, and ligand in the second increment because addition of only monomer did not cause additional growth of chains. A bimodal molecular weight distribution was observed having M_{n1} = 9400 g/mol, PDI_1 = 1.6 and M_{n2} = 102 400 g/mol, PDI_2 = 1.3 by GPC (see Figure 1). As the GPC illustrates, only a fraction of the chains were capable of additional growth.

End Group Analysis. The end groups of the acrylamide polymers were analyzed by MS (Figures 2 and 3). When initiator **1** was used in 9:1, toluene:DMF (theoretical M_n = 2500 g/mol), we observed molecular ion peaks (Figure 2) for the polymers shown in Scheme 2; conversion was 96%. The hydroxy-terminated material (m/z = 1146; $[EtOCOC(CH_3)_2-(DMA)_{10}-OH + Na]^+$) could have arisen from hydrolysis of the bromo compound[14] or hydrolysis of the products of nucleophilic displacement of the halide by an amide group.[8] We also observed products related to termination via disproportionation (m/z = 1130, $[EtOCOC(CH_3)_2-(DMA)_{10}-H + Na]^+$) and coupling ($m/z$ = 1145, $[EtOCOC(CH_3)_2-(DMA)_9-C(CH_3)_2CO_2Et + Na]^+$) reactions. When initiator **3** was used in 9:1 H_2O:dioxane (theoretical M_n = 2000 g/mol), we only observed a polymer corresponding to −OH termination (Figure 3); conversion was 90%. Heating **2** in water in the presence of CuX/ligand did not produce the corresponding hydroxy compound that would be expected from direct displacement of the bromide.

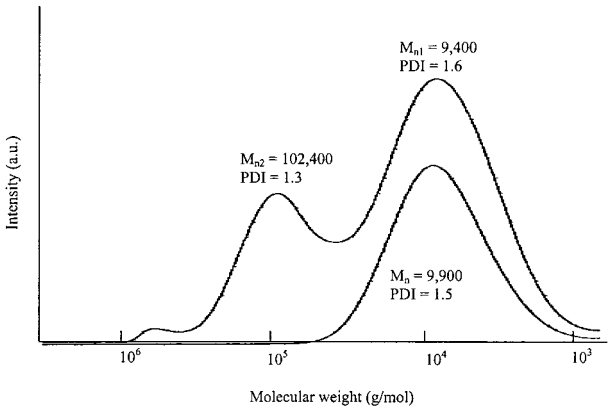


Figure 1. Gel permeation chromatography analysis of PDMA in sequential monomer addition experiment. Monomodal distribution corresponds to the first monomer addition, theoretical M_n = 2500 g/mol, and the bimodal distribution was obtained after the second monomer addition, theoretical M_n = 5000 g/mol.

Discussion

Our results for DMA polymerizations are similar to the published work of Teodorescu and Matyjaszewski.[8] We have also concluded that ATRP of DMA is not controlled. We observed similarly broad polydispersities and lack of agreement between experimental and theoretical M_n. The uncontrolled nature of ATRP of DMA also is confirmed by the polymer growth resumption experiment in which only a small fraction of the chain ends increased in molecular weight. In terms of mono-

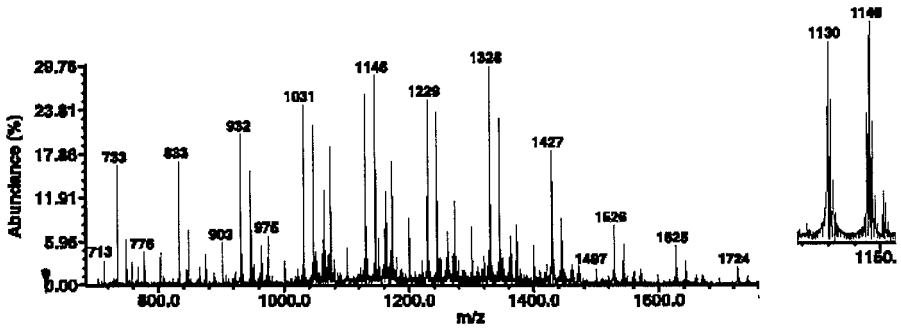


Figure 2. Electrospray MS analysis of product produced from DMA polymerization by initiator **1** in 9:1 toluene:DMF using ligand **6**; theoretical M_n = 2500 g/mol.

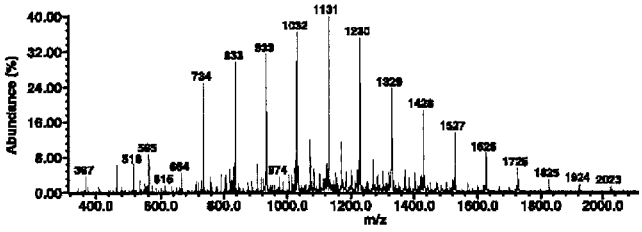
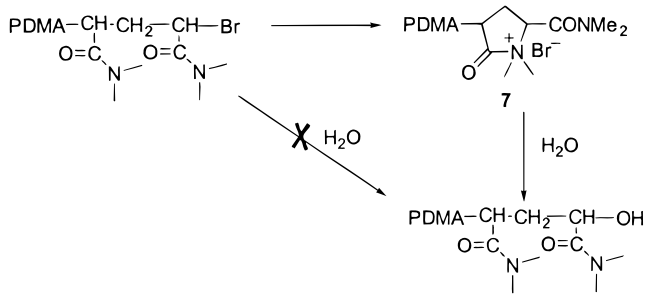


Figure 3. Electrospray MS analysis of product produced from DMA polymerization by initiator **3** in 9:1 H_2O:dioxane using ligand **4**; theoretical M_n = 2000 g/mol.

Scheme 3



mer conversion, our best results were obtained using the Me_4Cyclam ligand. Unlike Teodorescu and Matyjaszewski, we obtained high conversions (>90%). Similar to Matyjaszewski, using the Me_4Cyclam ligand, we were able to initiate many of the DMA polymerizations at room temperature using the Me_4Cyclam ligand (although as mentioned before, the polymerization exotherm effected an increase in reaction temperature). Changing the halide did not dramatically improve the polymerization.

We found that a variety of solvents could be used to obtain high DMA conversions including DMF, water, and toluene. Polymerizations conducted in water proceeded most rapidly. In fact, complete monomer conversions could be obtained in minutes. This is consistent with literature reports on the conventional radical polymerization of (meth)acrylamides where water exerts an accelerating effect on polymerization.[15] Of course, these fast reaction times are undesirable for controlled/"living" radical polymerization. An important mechanistic feature of controlled radical polymerizations is to maintain a low radical concentration in order to minimize spontaneous, bimolecular termination. Rapid polymerizations indicate a high concentration of radicals. A high, steady-state concentration of radicals is also consistent with the conclusion of Teodorescu and Matyjaszewski that deactivation of the poly(*N,N*-dimethylacrylamide) chain ends is too slow and cannot compete effectively with monomer addition.

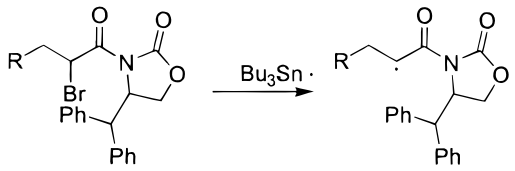
Interestingly, Wirth and co-workers[9] have claimed a living polymerization of acrylamide using ATRP with surface-immobilized initiators. The evidence for living polymerization was based on a correlation between film thickness and monomer concentration; also narrow molecular weight distributions were cited by Wirth and co-workers as evidence that their polymerization is living. A truer test of living behavior in Wirth's system would have been polymer growth resumption. It is possible that acrylamide behaves differently than DMA or that surface-initiated polymerizations are mechanistically different than solution polymerizations; however, on the basis of our work and that of Teodorescu and Matyjaszewski, we conclude that ATRP of (meth)acrylamides is not living.

Braslau, Hawker, and co-workers[16] successfully performed a living polymerization of DMA using an alkoxyamine. In addition to narrow molecular weight distributions (<1.15), they were able to control experimental M_n by varying the ratio of monomer/initiator. Le, Moad, Rizzardo, and Thang[17] also reported the living polymerization of DMA by a radical process using RAFT. They did not report extensive studies on DMA polymerization, but they achieved the same level of success as the nitroxide work. Both of these recent reports demonstrate that (meth)acrylamides can be successfully polymerized using living radical methods.

Teodorescu and Matyjaszewski offered several reasons why there is lack of control in the copper-mediated ATRP of (meth)acrylamides. These reasons include (1) inactivation of catalyst by polymer complexation, (2) strong bond between bromine and the terminal monomer unit in the polymer, and (3) nucleophilic displacement of terminal bromine by the penultimate amide group. Teodorescu and Matyjaszewski concluded that the first two reasons could not be solely responsible for lack of control in the polymerizations.

End group analysis via mass spectrometry indicated bimolecular termination products and hydroxy-functionalized polymer for polymerizations in toluene. For polymerizations in water, only the hydroxy-terminated polymer was observed. The bimolecular termination products are consistent with an excessively high concentration of radicals. We speculate that the origin of the hydroxy-functionalized polymer is from hydrolysis of the cyclized chain end (**7**), not the bromo-terminated polymer (see Scheme 3). We expect that **7** would be more susceptible to hydrolysis than the bromo-terminated chain end. We confirmed the hydrolytic stability of initiator **2** under typical polymerization conditions. The intervention of the cyclic onium intermediate **7** in the formation of hydroxy-terminated polymers is consistent with speculations of Teodorescu and Matyjaszewski.[8]

Scheme 4



The primary explanation given by Teodorescu and Matyjaszewski for an uncontrolled polymerization is slow deactivation of the chain ends. The organic literature contains support for this contention. Several examples have been reported of radical generation from alkyl bromides where the reaction is promoted by complexation of Lewis acids to amide bonds.[18] A particularly relevant example is that of Sibi and Ji[19] where alkyl bromide **8** (Scheme 4) is more readily transformed to the corresponding radical when a Lewis acid is present (e.g., $MgBr_2$ or a lanthanide). A similar example of this effect was observed by Porter and co-workers.[20] Both of these reports demonstrate that the presence of Lewis acid can have a profound effect on C−Br lability in chemical structures bearing an imide group alpha to the bromine. Using the reactivity−selectivity principle, we can conclude that the formation of C−Br bond from an amide-substituted radical will be less favorable in the presence of a Lewis acid. Because ATRP involves metals that can serve as Lewis acids, we conclude that it is the presence of the metal and its complexation to the amide functionality that slows deactivation in ATRP of (meth)acrylamides and makes the process an uncontrolled polymerization.

After completing this paper, Teodorescu and Matyjaszewski[21] disclosed a set of experimental conditions that produced narrow polydispersity poly(*N*,*N*-dimethylacrylamide). By using ligand **5**, CuCl, and methyl-2-chloropropionate, they reported polymer with a polydispersity of 1.11; the polymerizations were sluggish with 69% conversion after 26 h. While we did not use these exact conditions, we did perform similar polymerizations and still obtained broad polydispersities. These recent results of Teodorescu and Matyjaszewski will require examination and are the subject of current investigations.

Conclusions

After trying a variety of different experimental conditions, we have concluded that ATRP of *N*,*N*-dimethylacrylamide is not a controlled polymerization. This is based on broad molecular weight distributions, poor agreement between theoretical and experimental M_n, resumptive monomer addition experiments, and end group analysis. We believe that the Cu salts complex to the amide group of the chain ends and stabilize the radical. This stabilization retards the deactivation step in ATRP and produces an unacceptably high concentration of radicals which leads to spontaneous termination reactions. In addition, we have indirect evidence for a cyclization reaction involving nucleophilic Br displacement by the penultimate amide nitrogen; this cyclic onium intermediate undergoes hydrolysis to form a hydroxy-terminated polymer.

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