Atom Transfer Radical Polymerization of (Meth)acrylamides

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ABSTRACT: The polymerization of several (meth)acrylamides [*N*,*N*-dimethylacrylamide, *N*-*tert*-butylacrylamide, and *N*-(2-hydroxypropyl)methacrylamide] by atom transfer radical polymerization (ATRP) was attempted. When initiating systems containing ligands commonly used in ATRP, such as linear amines or bipyridines, were employed, very low conversions were noticed in either bulk or solution, after more than 20 h at 90 °C. However, the use of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam) as a ligand provided polymers in high yields in a short time, but the polymerization was not controlled. This was attributed to the slow deactivation rate of the catalytic system. Experiments using model compounds for the active chain ends indicated that the low conversion obtained in the polymerization of (meth)acrylamides when linear amines or bipyridines are used as ligands may be explained by a slow activation in conjunction with a fast deactivation. The loss of bromine end groups during the polymerization through a cyclization reaction could have a contribution to the poor control in the ATRP of (meth)acrylamides. Additionally, poly(meth)acrylamides may competitively complex copper and form species with lower catalytic activity. Even though the ATRP of (meth)acrylamides was not a controlled process, by using the Me_4Cyclam-based catalyst system and macroinitiators prepared by ATRP, poly(methyl acrylate-*b*-*N*,*N*-dimethylacrylamide) (M_n = 48 600, M_w/M_n = 1.33) and poly[butyl acrylate-*b*-*N*-(2-hydroxypropyl)methacrylamide] (M_n = 34 000, M_w/M_n = 1.69) block copolymers were synthesized.

Introduction

Polymers of acrylamide and its derivatives are widely used in industry, agriculture and medicine due to their remarkable properties including biocompatibility, lack of toxicity, water solubility, and so on. Among the most important applications of these polymers are flocculating agents for minerals, coal and industrial wastes, thickening and water clarifying agents, flooding agents for petroleum recovery, soil stabilizers and agents for water-loss prevention in soil, dental fillers and tumor suppressants, components of hair sprays and shaving creams, and many others.[1,2] The preparation of these polymers is based almost entirely on a free-radical mechanism. Anionic polymerization has been also applied, but in a much smaller extent, leading to vinyl polymers only for *N*,*N*-disubstituted acrylamides.[3−5]

(Meth)acrylamide-based homo- and block copolymers with low polydispersities and predetermined molecular weights can be very useful in many fields, but their synthesis would require the application of the "living"/controlled techniques. Until a couple of years ago, these techniques were restricted to the ionic and coordinative mechanisms, but free-radical methods have lately become available for the preparation of well-defined homo- and block copolymers. The main types of controlled/"living" radical polymerizations are (i) stable free radical polymerization (SFRP), which employs stable nitroxyl radicals;[6,7] (ii) atom transfer radical polymerization (ATRP), which uses complexes of transition metals such as copper,[8,9] ruthenium,[10] iron,[11,12] nickel,[13,14] and rhodium,[15,16] in conjunction with alkyl halides; and (iii) reversible addition−fragmentation chain transfer polymerization (RAFT), which uses dithioesters together with a free radical initiator.[17] These three techniques together allow for the polymerization in a controlled/"living" manner of most vinyl monomers, with the main exceptions being vinyl acetate and vinyl chloride.

Taking into account that their reactivity is similar to that of acrylates, the absence of (meth)acrylamides on that list is quite surprising. Although ATRP initiating system benzyl chloride/CuCl/2,2′-bipyridine was used to grow polyacrylamide films from a silica surface, the detailed proof for the controlled character of the polymerization was not provided.[18] SFRP of *N*,*N*-dimethylacrylamide (DMAA) was also attempted, but the process was not controlled/"living".[19] However, the authors were able to prepare homo- and block copolymers of DMAA with relatively low polydispersity.

In our continuing effort to expand the area of ATR polymerizable monomers, we investigated the polymerization of (meth)acrylamides. The monomers examined were DMAA, *N*-*tert*-butylacrylamide (*t*-BAA) and *N*-(2-hydroxypropyl)methacrylamide (HPMA). In this paper, we present our results concerning their polymerizability by copper-based ATRP and the preparation of some (meth)acrylamide-containing block copolymers.

Experimental Section

Materials. Methyl acrylate (MA) and butyl acrylate (BA) from Acros were vacuum distilled over CaH_2. *N*,*N*-Dimethylacrylamide (DMAA, Aldrich) was distilled under vacuum. *N*-*tert*-Butylacrylamide (*t*-BAA, Aldrich) was recrystallized from benzene. *N*-(2-Hydroxypropyl)methacrylamide[20] was provided by Prof. J. Kopecek from the University of Utah, and it was used as received. All monomers were stored at −15 °C after purification. Methyl 2-bromopropionate (MBP, Aldrich) was distilled under vacuum. *N*,*N*-Dimethyl-2-bromopropanamide (BrDMAA) and 2-*N*,*N*-trimethyl-2-bromopropanamide (BrDMMA) were synthesized from the corresponding acid bromide and dimethylamine hydrochloride, in the presence of NaOH.[21,22] 1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam), *N*,*N*,*N*′,*N*′,*N*″-pentamethylethylenetriamine (PMDETA), and 2,2′-bipyridine (bpy) from Aldrich were used as received. CuBr (98%, Aldrich) was purified according to the published procedure.[23] All of the solvents were used without further purification. In many cases, monomers and

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Table 1. Polymerization of DMAA with Different Ligands at 90 and 110 °C[a]

catalytic system	temp. (°C)	time (h)	conv. (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
CuBr:PMDETA	110	45	4	400	59 300	2.02
MBP:CuBr:PMDETA	90	24	5	500	600	1.19
	110	6	5	500	54 800	2.39
		23.3	28	2800	74 100	2.46
		45	45	4500	65 300	2.94
MBP:CuBr:bpy	110	22.5	0			

[a] Experimental conditions: $[DMAA]_o = 9.7$ M (bulk); $[MBP]_o = 0.97$ mM; $[CuBr]_o = 0.97$ mM; $[PMDETA]_o = 0.97$ mM; $[bpy]_o = 2.91$ mM.

solvents were bubbled with argon for at least 15 min immediately before polymerization.

Polymerizations. *Single-Point Experiments.* A glass tube was loaded with all of the solid compounds (CuBr, Me_4Cyclam, *t*-BAA, and HPMA), capped with a rubber septum, and cycled three times between vacuum and argon to remove oxygen. Then, all of the liquid components (monomer, solvent, GC standard, ligand, and initiator), previously degassed, were added via syringe. The tube was sealed under argon and placed in an oil bath thermostated at the desired temperature. After a certain time interval, the tube was cooled in an ice−water mixture and then opened, and the contents were dissolved in dimethylformamide (DMF) or tetrahydrofuran (THF).

Kinetic Experiments. A Schlenk flask was charged with CuBr and the other solid compounds. The flask was sealed with a rubber septum and was cycled three times between vacuum and argon to remove oxygen. The degassed liquid components, except for the initiator, were added through degassed syringes, and the mixture was stirred at room temperature until the catalytic complex formed. The flask was then placed in an oil bath kept at the desired temperature, and the initiator was added. After certain time intervals, samples were withdrawn from the reaction mixture using degassed syringes and dissolved in DMF or THF.

Measurements. Monomer conversion was determined by GC using chlorobenzene (MA, DMAA, and *t*-BAA) or diphenyl ether (HPMA) as internal standards. A Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column with a Shimadzu CR501 chromatapac was used. Polymer samples, dissolved in THF (PMA and PtBAA) or DMF (PDMAA, PHPMA, and block copolymers) were passed through an alumina column to remove copper. Molecular weights and molecular weight distributions were measured using a Waters 712 WISP autosampler and PSS guard and 10^5, 1000, and 100 Å columns in THF for PMA and P*t*-BAA; a Waters U6K injector and Phenogel 5×10^4 Å, PSS 1000 Å and PSS 100 Å columns in DMF for PDMAA, PHPMA, and block copolymers. In both cases, a Waters 410 differential refractometer was used. ^{1}H NMR spectra were measured in DMF-d_7 (PBA-*b*-PHPMA) or DMSO-d_6 (PMA-*b*- PDMAA) on a Bruker AM 300 MHz spectrometer.

Results and Discussion

Preliminary Experiments. Experiments have been performed under various conditions to polymerize several (meth)acrylamide monomers. Ligands commonly used in ATRP such as linear amines[24] or substituted and unsubstituted bipyridine,[8,9,25] in conjunction with CuBr afforded only very low conversions, either in bulk or solution, after more than 20 h at 90 °C, confirming Li and Brittain's results.[19] Bipyridine-based copper complexes failed to initiate the polymerization even at 110 °C, while at the same temperature, PMDETA as a ligand led to a higher yield, but the polymerization was slow and uncontrolled, although much faster than the thermally initiated process (Table 1).

However, when Me_4Cyclam was used as ligand, higher conversions in relatively shorter times were observed (Table 2). Even though the experimental molecular weights were higher than the theoretical values and the polydispersities were quite large, indicating uncontrolled polymerizations, we decided to investigate more deeply this catalytic system, hoping to understand the reason for the difficulties encountered in applying ATRP to acrylamides.

Table 2. Polymerization of (Meth)Acrylamides Investigated Using Me_4Cyclam as Ligand[a]

monomer	time (h)	conv. (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
HPMA	2.5	76	3800	20 100	1.7
t-BAA	1	94	9400	10 700	2.9
DMAA	8	62	6200	10 000	1.8

[a] Experimental conditions: monomer/solvent = 1/3 (wt/vol); target M_n = 5000 (HPMA), 10000 (*t*-BAA, DMAA); initiating system = MBP:CuBr:Me_4Cyclam = 1:1:1; temp = 90 °C; solvent = 1-butanol (HPMA) and methanol (*t*-BAA, DMAA).

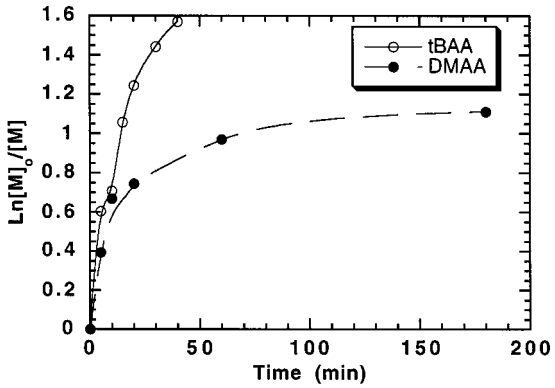


Figure 1. Kinetic plot for the solution polymerization of *t*-BAA and DMAA using Me_4Cyclam as the ligand. Experimental conditions: 0.5 g monomer/1.5 mL methanol; MBP:CuBr:Me_4Cyclam = 1:1:1; *t*-BAA:MBP = 78.74; DMAA:MBP = 101; 18 °C.

Polymerizations Using Me_4Cyclam as a Ligand. Me_4Cyclam-based initiating systems promoted a very fast polymerization of both DMAA and *t*-BAA even in solution at room temperature (Figure 1). The conversion increased rapidly at the beginning of the reaction in both cases but leveled off at about 65% for DMAA. Curvature of the first-order kinetic plots was noticed in both cases, indicating that termination had occurred during the reaction. This fact, together with the decrease of molecular weights with conversion (Figure 2), indicate the presence of chain breaking reactions and a mechanism similar to conventional redox-initiating systems.

In a regular ATRP, the addition of small amounts of deactivating CuX_2 slows the reaction, improving the control of molecular weights and polydispersities.[26] In the case of DMAA polymerization with the Me_4Cyclam-based catalytic system, the addition of $CuBr_2$ decreased the final conversion, molecular weight, and polydispersity, but still, there was poor agreement between experimental and theoretical M_n, and the molecular weight distribution was too large for a controlled polymerization (Table 3). To understand better the initiating system containing Me_4Cyclam as a ligand, it was employed in polymerization of methyl acrylate, which is known to be an ATR polymerizable monomer[9,26] (Figures 3 and 4).

Even though the first-order kinetic plot was not linear, due to the slow initiation at room temperature (Figure 3), the polymerization displayed some, but not

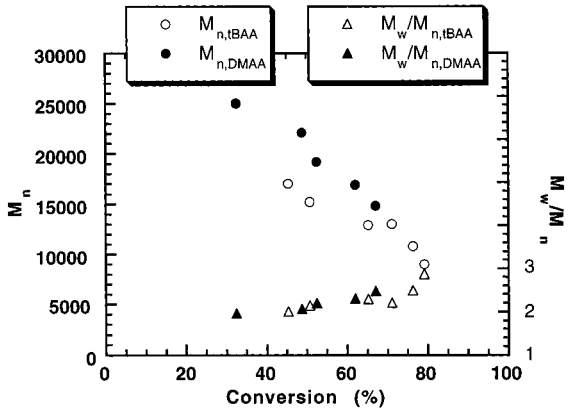


Figure 2. Dependence of molecular weight, $M_{n,SEC}$, and molecular weight distribution, M_w/M_n, on monomer conversion for the solution polymerization of *t*-BAA and DMAA using Me_4Cyclam as the ligand. Experimental conditions: 0.5 g monomer/1.5 mL methanol; MBP:CuBr:Me_4Cyclam = 1:1:1; *t*-BAA:MBP = 78.74; DMAA:MBP = 101; 18 °C.

Table 3. DMAA Polymerization with Me_4Cyclam-Based Catalytic System in the Presence of Added Amounts of $CuBr_2$[a]

$CuBr_2$/CuBr mol/mol	conv. (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
0	62	6200	12700	1.79
0.2	44	4400	8200	1.73
0.4	38	3800	7100	1.65

[a] Experimental conditions: solvent = methanol; $[DMAA]_o = 2.5$ M; $[MBP]_o = 24.7$ mM; $[CuBr]_o = 24.7$ mM; (CuBr+$CuBr_2$): Me_4Cyclam = 1:1; 50 °C; reaction time = 3 h.

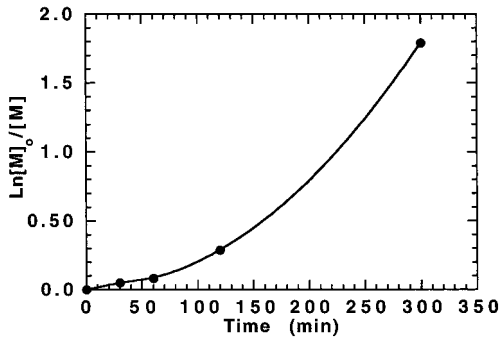


Figure 3. Kinetic plot for the bulk polymerization of MA using Me_4Cyclam as the ligand. Experimental conditions: $[MA]_o = 11.1$M; $[MBP]_o = [CuBr]_o = [Me_4Cyclam]_o = 47.7$ mM; 19 °C.

all, of the characteristics of a controlled process. That is, the molecular weights increased linearly with conversion, but they were higher than the theoretical values (Figure 4). Polydispersity was quite high, and it decreased with conversion, supporting the supposition regarding the slow initiation. The molecular weight corresponding to the peak maximum on the size exclusion chromatography (SEC) chromatogram (M_p) reached a very high value from the very beginning of the polymerization and then increased parallel with M_n.

These results can be explained by slow deactivation for the Me_4Cyclam system. Because of the slow deactivation, the molecular weight increases rapidly at the beginning of the MA polymerization, as M_p values show, and significant termination occurs. As a consequence, large amounts of $CuBr_2$ form, shifting the activation−deactivation equilibrium toward the dormant species and decreasing the concentration of propagating radicals. Consequently, the reaction slows down and control

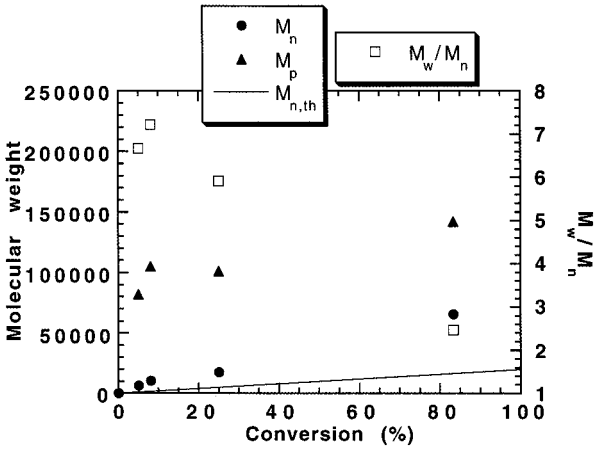


Figure 4. Dependence of molecular weight, $M_{n,SEC}$, peak maximum, $M_{p,SEC}$, and molecular weight distribution, M_w/M_n, on monomer conversion for the bulk polymerization of MA using Me_4Cyclam as the ligand. Experimental conditions: $[MA]_o = 11.1$M; $[MBP]_o = [CuBr]_o = [Me_4Cyclam]_o = 47.7$ mM; 19 °C.

improves, leading to the increase of the molecular weights and the decrease of the polydispersity (Figure 4). However, the experimental M_n's are higher than the theoretical values due to the loss of active species by termination at the beginning of the reaction.

Slow deactivation can also explain why high conversions of (meth)acrylamides can be reached when Me_4Cyclam is used as a ligand, but other ligands, such as bpy or PMDETA, which were successfully employed in ATRP of styrene and (meth)acrylates, afford only very low conversions. For reasons which will be presented later in this paper, the polymerization of (meth)acrylamides slows down dramatically or even stops after a couple of activation−deactivation cycles. Thus, conversions are very low in catalytic systems with fast deactivation; only a few monomer units are inserted before the chain stops growing. The Me_4Cyclam-based catalyst system affords the incorporation of a large number of monomer units into the polymer chain before deactivation or termination take place, resulting in higher conversions. Higher concentrations of $CuBr_2$ improve polydispersity by diminishing the recombination or disproportionation termination reactions and decrease both molecular weight and conversion (Table 3).

Plausible Reasons for the Lack of Control in Copper-Mediated ATRP of (Meth)acrylamides. The lack of control in copper-mediated ATRP of (meth)acrylamides can be explained by several reasons, which are discussed separately below.

1. Inactivation of the Catalyst by Complexation of Copper by the Forming Polymer. Polyacrylamides, as well as the parent monomers, complex transition-metal cations[1,27,28] through the amide group. The polymer complexation constant may be stronger due to the large local concentration of complexing groups allowing polydentate interactions. Therefore, the forming polymer may competitively bind copper, thus removing it from its complex with the original ligand, and slow or even stop polymerization. Me_4Cyclam, because of its cyclic structure, has a complexation constant for transition metals much higher than that of the open-chain ligands,[29] and therefore, it may not be removed as easily by the polymer from its copper complex.

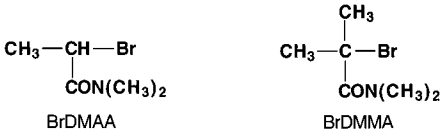
To check this supposition, ATRP of MA was carried out in bulk in the presence of 10 wt % poly(*t*-BAA) (Table

Table 4. MA Polymerization in the Presence of Poly(*t*-BAA)[a]

expt.	conv. (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
A	90	18 000	18 800	1.07
B	68	13 600	11 200	1.14
C	2			

[a] Experimental conditions: bulk, $[MA]_o$ = 11.1M; $[MBP]_o$ = 47.7mM; $[CuBr]_o = [PMDETA]_o$ = 23.9mM; 80 °C; 20 h. A, blank experiment with no poly(*t*-BAA) added; B, poly(*t*-BAA) (M_n = 9900, M_w/M_n = 2.97) added 10 wt % based on MA; and C, poly(*t*-BAA) added and no initiator.

Scheme 1



4). Indeed, MA polymerized to a lower conversion in the presence of poly(*t*-BAA), but the process was well-controlled, as proved by the low polydispersity of obtained polymers (Table 4, expts A and B).

Poly(*t*-BAA) employed in these experiments was prepared by ATRP using Me_4Cyclam as a ligand. When it was used as a macroinitiator in MA polymerization (Table 4, expt C), block copolymerization was unsuccessful, resulting in only 2% MA consumption. This may suggest that either the terminal C−Br bond in poly(*t*-BAA) is too strong to be efficiently activated under the applied conditions, indicating slow initiation (cf. subsection 2), or that there is no such group available (cf. subsection 3).

As the polymerization of (meth)acrylamides catalyzed by linear amines and bipyridines usually reaches conversions lower than 10%, the above result indicates that complexation of copper is not the only reason for the lack of polymerizability of these monomers. At higher concentrations of polymer in the reaction mixture, i.e., higher conversions, the displacement of copper from its complex by the polymer will be more favored. The conversion at which the phenomenon occurs should depend on the complexation constant of the ligand employed. A ligand with a higher complexation constant should require a higher amount of polymer to be removed from its complex, which means that a higher conversion can be reached.

2. Strong Bond between the Terminal (Meth)acrylamide Unit in Polymer and the Bromine Atom. To verify this supposition, small-molecule models for the dormant species in ATRP of (meth)acrylamides were synthesized (Scheme 1). BrDMAA is a model for the active centers in DMAA polymerization, whereas BrDMMA comes from *N*,*N*-dimethylmethacrylamide, and it represents a model for the polymerization of methacrylamides. These two model compounds were employed as initiators for the MA polymerization catalyzed by CuBr complexed with Me_4Cyclam and PMDETA (Table 5).

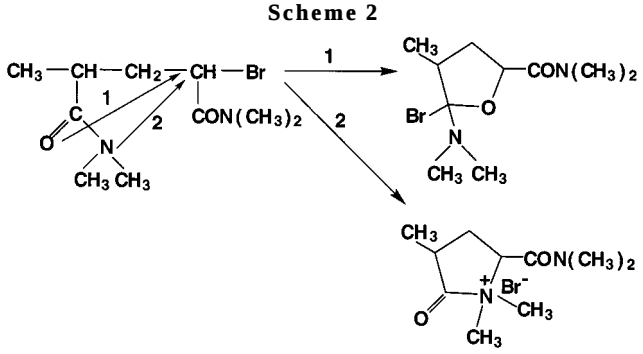
The results showed that the amide−Br group can be activated by both Me_4Cyclam and PMDETA. When Me_4Cyclam was used as a ligand, the polymerization was very fast and uncontrolled at 50 °C for both initiators. Polymers with very high polydispersities were obtained, and the molecular weights were much higher than the theoretical values. On the other hand, the use of PMDETA as a ligand afforded a controlled polymerization of MA for both model compounds at 50 and 80 °C, but it was much slower than in the case of MBP as

Table 5. Methyl Acrylate Polymerization Initiated by BrDMAA and BrDMMA[a]

initiator	ligand	temp (°c)	time (h)	conv. (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n
BrDMMA	Me_4Cyclam	50	0.17	95	9500	19 300	4.09
BrDMMA	PMDETA	50	22.5	13	1300	2 360	1.87
BrDMMA	PMDETA	80	22	71	7100	7 500	1.25
BrDMAA	Me_4Cyclam	50	1	83	8300	14 700	8.44
BrDMAA	PMDETA	50	22.5	31	3100	4 200	1.53
BrDMAA	PMDETA	80	23	68	6800	7 900	1.46
MBP	PMDETA	50	5	74	7400	7 100	1.10
MBP	PMDETA	80	1.62	81	8100	8 900	1.09
	PMDETA	80	23	17		16 3000	1.43

[a] Experimental conditions: bulk, $[MA]_o$ = 11.1M; $[initiator]_o = [CuBr]_o = [ligand]_o$ = 95.5mM.

Scheme 2



initiator. The conversion was higher than for the thermal polymerization (68−71% vs 17% at 80 °C), indicating the contribution of the added initiators. The obtained molecular weights agreed relatively well with the expected values, but the polydispersities were higher than in the case of MBP. The polymer peaks on the SEC chromatograms showed long tails in the low-molecular-weight region. These observations suggest a slow initiation due to a stronger C−Br bond for (meth)acrylamides than that for (meth)acrylates. This indicates that the ATRP equilibrium constants are significantly lower for (meth)acrylamides than for (meth)acrylates. Therefore, the slow rates observed in the polymerization of (meth)-acrylamides catalyzed by copper complexed with linear amines or bipyridines may be partially explained by a very slow activation in conjunction with a fast deactivation. Complexes with more reducing properties may enhance the rate of the activation step and enable the preparation of polyacrylamides in a higher yield. However, a stronger C−Br bond cannot explain the termination reactions observed in Figure 1.

3. Nucleophilic Displacement of the Terminal Bromine Atom by the Amide Group. In addition to the slow activation step and complexation, the control of the polymerization can be affected by the loss of terminal bromine atoms due to cyclization reactions. They resemble the formation of onium ions in the cationic ring opening polymerization of oxazolines.[30] The terminal halogen atom may be displaced by the nucleophilic attack of either the carbonyl oxygen or the nitrogen atom of the amide group of the penultimate (meth)-acrylamide unit (Scheme 2). The reactions result in the formation of five-membered rings and can be entropically favored by the inherently close proximity of the penultimate amide unit to the C−Br group. The newly formed cyclic end groups can no longer be activated by the copper complexes used in ATRP. The displacement reaction should be faster for bromine than for chlorine and faster in polar solvents than in nonpolar ones, as well as accelerated at higher temperatures.

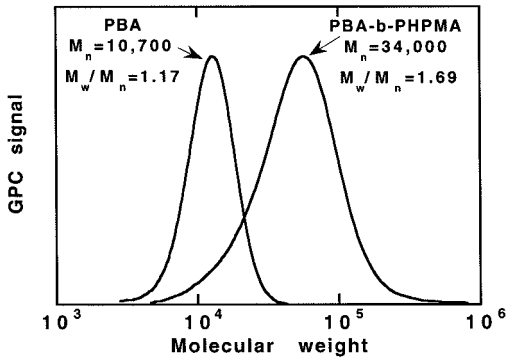


Figure 5. Molecular weight distributions of PMA macroinitiator and PMA-*b*-PDMAA block copolymer. Experimental conditions: DMAA:PMA:CuBr:$CuBr_2$:Me_4Cyclam = 238:1:1:0.1:1.1; solvent = methanol:ethyl acetate 1:1 (v/v); 50 °C; time = 5 h.

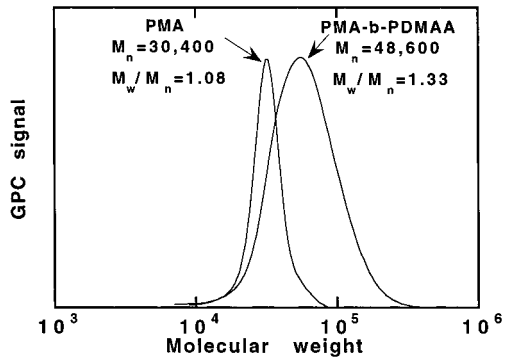


Figure 6. Molecular weight distributions of PBA macroinitiator and PBA-*b*-PHPMA block copolymer. Experimental conditions: HPMA:PBA:CuBr:$CuBr_2$ = 140:1:1:0.2:1.2; solvent = ethanol; 50 °C; time = 18 h.

(Meth)acrylamide-Based Block Copolymers. Even though the ATRP of (meth)acrylamides is not controlled/"living", it allowed for the preparation of block copolymers. Well-defined poly(methyl acrylate) (PMA) and poly(butyl acrylate) (PBA) were prepared by ATRP, purified, and used as macroinitiators for the polymerization of HPMA (Figure 5) and DMAA (Figure 6), respectively, with the CuBr/Me_4Cyclam catalytic system.

The GPC traces show that the polymerization of the second block was initiated quantitatively. However, despite the addition of $CuBr_2$ to the reaction mixture, the polydispersity of both block copolymers increased, especially for PBA-*b*-PHPMA, indicating a broad distribution of the second block. The M_n's of the block copolymers using PMMA standards for SEC calibration in DMF, were overestimated. ^{1}H NMR measurements showed a HPMA/BA molar ratio of 0.65 for PBA-*b*-PHPMA, meaning that the actual M_n of the block copolymer is about 18 000, rather than 34 000 as estimated from SEC. On the other hand, for PMA-*b*-PDMAA the ^{1}H NMR analysis showed a DMAA/MA ratio of 0.47, corresponding to a molecular weight of the block copolymer of 47 000, which agreed relatively well with the value determined by SEC (M_n = 48 600).

Conclusions

Attempts to polymerize DMAA, *t*-BAA, and HPMA by ATRP led to low conversions in either bulk or solution when ligands commonly used in ATRP, such as linear amines or substituted and unsubstituted bipyridines, were used. However, the Me_4Cyclam-based catalytic system was able to provide polymers in high yields in short times, due to the slow deactivation in this system. The polymerizations, however, were poorly controlled. The addition of $CuBr_2$ to the reaction mixture decreased the polydispersity by increasing the deactivation rate and reducing biradical termination. The low conversion obtained in the polymerization of (meth)acrylamides when linear amines or bipyridines are used as ligands may be explained by a slow activation in conjunction with a fast deactivation, indicating the inadequate redox potential of these catalysts. The loss of bromine end groups during the polymerization through a cyclization reaction may also contribute to the poor control in the ATRP of (meth)acrylamides. Additionally, polyacrylamides may competitively complex copper and form species with lower catalytic activity. Even though the ATRP of (meth)acrylamides is not a controlled/"living" process, it has been employed for the preparation of block copolymers such as PMA-*b*-PDMAA and PBA-*b*-PHPMA, by using polyacrylates prepared by ATRP as macroinitiators.

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