Living Radical Polymerization. 1. The Case of Atom Transfer Radical Polymerization of Acrylamide in Aqueous-Based Medium

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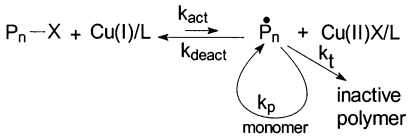
ABSTRACT: Atom transfer radical polymerization (ATRP) of acrylamide has been carried out in water or in glycerol−water (1:1 v/v) medium at 130 °C using water-soluble initiators, viz. 2-chloropropionamide (2-Cl-PA) or 2-bromopropionamide (2-Br-PA) and CuX (X = Cl, Br) bipyridine complex as catalyst. Extraneous addition of CuX_2 (20 mol % of CuX) and/or excess X^- ions (1 M alkali halide) in the reaction mixture helps to reduce molecular weight polydispersity (PDI). However, even under the best conditions (using both CuX_2 and X^- ion additives), the PDI is high, ca. 1.6−1.7. Also, the GPC traces show shoulders. The chain extension experiment, however, confirms the living nature of the polymers. Replacement of glycerol−water with water as the medium results in sluggish polymerization. The ln M_0/M vs t plots are curved to start with but become linear after polymerization proceeds to variable extents depending on the additives used. The molecular weights tend to agree with the theoretical values as conversion increases. A method of selecting the appropriate ligand for ATRP has been proposed on the basis of the premise that a high rate of deactivation is one of the primary requirements for ATRP to succeed. A relative measure of the deactivation rate for various ligands has been obtained from the molecular weights (GPC) of polymers formed in a CuX_2L_x deactivated polymerization initiated by an azo initiator at 90 °C. A ligand that leads to the highest deactivation rate has been proposed to be chosen.

Introduction

Recent years have witnessed significant progress in the field of living radical polymerization.[1−6] The latter uses a polymerization system in which the growing polymer chain end remains in a dynamic equilibrium between active and dormant species as a result of rapid, reversible termination or reversible degenerative chain transfer reaction. The propagation and reversible termination or transfer reaction should be much faster than any irreversible termination. In addition, if the initiation is also very fast, the process yields polymer with narrow molecular weight distribution.[7,8] The available methods are (i) nitroxide mediated stable free radical polymerization (SFRP),[9−11] (ii) transition metal complex mediated atom transfer radical polymerization (ATRP),[12−16] and (iii) degenerative transfer reaction with alkyl iodides[17−19] or reversible addition−fragmentation chain transfer polymerization (RAFT).[20,21] Of the above methods, ATRP has been very widely practiced.

ATRP uses a catalytic amount of a transition metal complex, which reversibly abstracts a halogen atom from a polymer chain end, thereby transforming the latter into an active propagating radical from a dormant state. The process is usually represented by the dynamic equilibrium shown in eq 1 for Cu complex as catalyst:[4]



(1)

where P_n represent a polymer chain containing n monomer units, $\dot{P}_n$ is the corresponding polymer radical, and P_n−X is the halogen terminated dormant polymer molecule. The equilibrium point in eq 1 should lie largely toward the left-hand side. This condition ensures that only a very low steady state concentration of chain radical is maintained such that their bimolecular termination is minimized. A large number of monomers with only a few exceptions have been successfully polymerized by this process, yielding polymers of predetermined chain length, low polydispersity, and well-defined chain ends. Besides, block copolymers have been prepared by sequential polymerization of different monomers.[1−6]

Among the notable monomers not satisfactorily amenable to ATRP are the (meth)acrylamides.[22−24] Some success is however reported with these monomers. Thus, Teodorescu and Matyjaszewski obtained polymers with low polydispersity and linear increase of molecular weight with conversion using the CuCl/hexamethyltris-(2-aminoethyl)amine (Me_6TREN) catalyst system. The conversion was of course limited, and a nonlinear ln M_0/M vs t plot was obtained (where M and M_0 are the monomer concentrations at time t and 0, respectively)[24] which was attributed to catalyst deactivation. Senoo et al. used a ruthenium chloride-based initiating system and obtained living polymers with controlled molecular weight and PDI = 1.6.[25]

As far as acrylamide is concerned, Huang and Wirth obtained polyacrylamide (PAM) with a PDI value of 1.11 when ATRP of acrylamide was carried out in DMF at 130 °C using benzyl chloride initiator and CuCl/bipyridine catalyst[26] which we could not reproduce (vide infra). Apart from PDI and the molecular weight distribution curve, these workers did not look into the other diagnostic features of ATRP, viz., linearity of ln M_0/M vs t plot and proportionality of molecular weight with conversion. Their primary interest was of course growing polymer film on solid surfaces through ATRP initiators bound to the surface.[26−28] They obtained linear increase in film thickness with acrylamide concentration, but not with time. Also, the polymer growth leveled off after about 10 h. While this work was completed,

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another publication of Xia and Wirth appeared in which they reported surface initiated ATRP of acrylamide at room temperature using CuCl/$CuCl_2$/Me_6TREN instead of the CuCl/bipyridine catalyst system which was used in their earlier work reported above.[29]

Various reasons have been put forward to explain the unsatisfactory ATRP of (meth)acrylamides. Among these are (1) the poly(meth)acrylamides may form strong complexes with the transition metal ions rendering the catalyst inactive. However, Teodorescu and Matyjaszewski found that ATRP of methyl acrylate proceeded satisfactorily albeit at a slower rate in the presence of 10 wt % added poly(*tert*-butyl acrylamide).[22] (2) The bond between the terminal (meth)acrylamide residue in the polymer and the halide atom may be very strong so that activation is very slow. However, small molecular weight model initiators show that the former can be successfully used as initiators for ATRP of methyl acrylate using pentamethyldiethylenetriamine (PMDETA) ligand although the initiation is slower than with methyl bromopropionate. With some cyclic amine ligands, however, polymerization was very fast but uncontrolled.[22] (3) The halide atom from the polymer chain end may be removed due to a nucleophilic attack by either the carbonyl oxygen or the N atom of the amide group of the penultimate (meth)acrylamide unit. The effect would be more prominent with Br than with Cl atom.[22,23]

In this paper we have studied the ATRP of acrylamide in detail and worked out reaction conditions which help lower the polydispersity and get better agreement of molecular weight with theoretical values. Evidence of living nature of the polymers has been provided through chain extension experiments.

Experimental Section

Materials. Acrylamide (99+% electrophoresis grade, Sigma), glycerol (G.R. 99%, E Merck), and the ligands tetramethylethylenediamine (TMEDA, 99%), pentamethyldiethylenetriamine (PMDETA, 99%), hexamethyltriethylenetetraamine (HMTETA, 98%), bipyridine (bpy, 99+%) (all Aldrich products), and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4-cyclam, 98%, Acros), were used as received. CuBr (98%, Aldrich) and CuCl (98%, BDH) were purified by washing with the corresponding acids (10% HX in water) followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. Commercial distilled water was redistilled over alkaline permanganate. 2-Chloropropionamide (2-Cl-PA) and 2-bromopropionamide (2-Br-PA) were synthesized following the procedure for the synthesis of chloroacetamide.[30]

Polymerization. Polymerization was conducted in 8 cm × 2.5 cm test tubes provided with B-19 standard joints. The test tubes were closed with rubber septums which were secured by Cu wires. Before polymerization the reaction mixture was purged with oxygen-free nitrogen for 40 min. The pH at the start for all polymerization recipes was adjusted to 8.5 by adding alkali, if necessary. Samples were withdrawn from time to time using gastight syringes, and the polymer precipitated into methanol. The precipitated polymer was separated by centrifugation, redissolved in a minimum amount of water, and reprecipitated into methanol. This step was done to free the polymer from any entrapped glycerol. The polymer was dried in a vacuum oven at 45 °C for 48 h. Polymerization in water at 130 °C was conducted in sealed tubes.

An example for polymerization with the 2-Cl-PA/CuCl/bpy system is as follows. In an above-mentioned test tube was taken 3 mL of glycerol−water mixture (1:1 v/v) which was then purged with nitrogen for 15 min. LiCl (132 mg, 3.18 mmol), AA (900 mg, 12.67 mmol), $CuCl_2 \cdot 2H_2O$ (2.05 mg, 0.012 mmol), CuCl (5.94 mg, 0.06 mmol), and bipy (22.5 mg, 0.144 mmol) were added sequentially at room temperature under nitrogen. After a further 15 min of nitrogen purge, 2-Cl-PA (6.5 mg, 0.06 mmol) was added to the admixture. The reaction vessel was sealed by a rubber septum which was secured by Cu wire and placed in an oil bath maintained at a temperature of 130 °C. After 25 h reaction time 71% conversion was reached. The $\bar{M}_n$ and PDI of the obtained polymer were 12 500 and 1.5, respectively. NMR data: CH_2 (t, δ = 1.69, 2H), CH($CONH_2$) (unresolved, δ = 2.23, 1H).

Two-Stage Monomer Addition Polymerization. The first stage was the same as described in the above paragraph. After the first stage of polymerization for 25 h 1.2 mL of polymerization mixture was withdrawn using a gastight syringe. The polymer was isolated by precipitation into methanol and characterized. A fresh solution of monomer (450 mg, 6.33 mmol) in 1.2 mL of aqueous glycerol (50 vol %) previously purged with nitrogen was introduced into the reaction tube under nitrogen using the syringe. The polymerization was then continued for a further period of 25 h. The polymer was then isolated and characterized. It should be noted that the concentrations of CuCl, $CuCl_2$, bpy, and LiCl in the second stage were 60% of those used in the first stage.

Characterization. The molecular weight distribution (MWD) was determined by GPC at room temperature (ca. 30 °C) using a Waters model 510 HPLC pump, a Waters series 400 differential refractometer, and three Waters Ultrahydrogel columns of 500, 250, and 120 Å pore size and 10, 6, and 6 μm bead size, respectively, which were preceded by an Ultrahydrogel guard column. An aqueous solution of 0.1 M $NaNO_3$ was used as eluant at a flow rate of 0.5 mL/min. Before injection into the GPC system the polymer solutions were treated with cation-exchange resin Dowex 50W (Fluka) to free them from Cu salts. They were then filtered through a prefilter−filter combination system compatible with aqueous solutions. Poly(ethylene glycol) and poly(ethylene oxide), obtained from Waters, were used as calibration standards. However, since the hydrodynamic volumes of the standards are not likely to be the same as those of PAM of same molecular weights, the GPC traces were used only to calculate the PDI. The actual molecular weights were measured by the viscometric method for which the intrinsic viscosity was determined by the single point method using eq 2.[31] The viscosity was determined using 0.5 M NaCl as the solvent at 25 °C.

$$[\eta] = \frac{\sqrt{2\eta_{sp} - 2\ln \eta_{rel}}}{C} \tag{2}$$

The weight-average molecular weight ($\bar{M}_w$) was calculated using the following Mark−Houwink relation.[32]

$$[\eta] = 7.19 \times 10^{-5} \bar{M}_w^{0.77} \tag{3}$$

The constants in the above equation were determined by Klein and Conrad using unfractionated polyacrylamide samples whose molecular weights were determined by the light scattering method.[32] The number-average molecular weight $\bar{M}_n$ was calculated from $\bar{M}_w$ using the PDI values of the samples determined from the GPC traces.

Nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Bruker spectrometer using a 0.05% solution of the polymer in D_2O at 90 °C and sodium 3-(trimethylsilyl)-propionate as reference.

Results

1. Screening of Ligands. In ATRP a variety of nitrogen-based ligands have been used,[4,5] e.g., multidentate linear amines, bipyridine (bpy), tripodal amines (e.g., TREN or Me_6TREN), cyclic amines (e.g., cyclam, Me_4cyclam), alkylpyridyl methanimines,[33,34] etc.

As far as (meth)acrylamide polymerizations are concerned, use of linear amines or bipyridines gave very poor yields even after 24 h reaction time at 90 °C

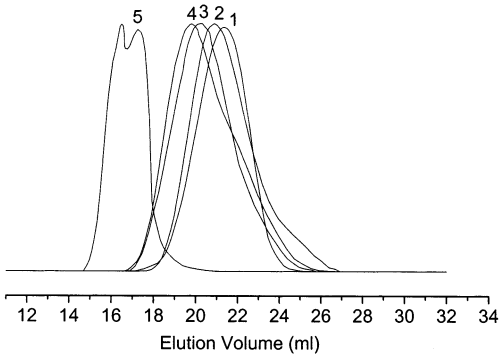


Figure 1. GPC traces of PAM obtained in the free radical polymerization of acrylamide in water at 90 °C in the presence of $CuCl_2$ complexed with various ligands: [acrylamide] = 2.11 M; [ACPA] = 2×10^{-4} M; [$CuCl_2$] = 0.008 M; $CuCl_2$:L = 1:2.5. Curves 1 through 5 are for ligands bpy, PMDETA, HMTETA, TMEDA, and Me_4 cyclam, respectively.

whereas with Me_4cyclam ligand polymerization was very fast but uncontrolled. The latter was attributed to the slow rate of deactivation (eq 1).[22] On the other hand, with Me_6TREN and chlorine-based catalyst initiator system some of the attributes of ATRP (like linear increase of molecular weights with conversion, low PDI) were observed, but the conversion was limited.[24]

One of the selection criteria for the ligand could be a fast deactivation rate (eq 1).[5] A screening of different ligands may therefore be possible by a comparative study of the effect of these ligands on the molecular weights of polymers obtained in the Cu(II)X_2L_x deactivated solution polymerization of acrylamide initiated by a water-soluble azo-initiator, e.g., 4,4′-azobis(4-cyanopentanoic acid) (ACPA). Figure 1 shows the GPC traces of PAM prepared by polymerizing for the same time a 2.11 M acrylamide solution in water at 90 °C using 2×10^{-4} M ACPA and complexes of $CuCl_2$ (8×10^{-3} M) with various ligands as chain terminators with $CuCl_2$:L = 1:2.5 where L = PMDETA, bpy, HMTETA, TMEDA, and Me_4cyclam. The figure clearly reveals that the molecular weight of PAM follows the following order for the ligands Me_4cyclam > TMEDA > HMTETA > PMDETA > bpy. Thus, the deactivation rate is slowest with Me_4-cyclam and highest with bpy. The slow deactivation rate with Cu(II) Me_4cyclam complex is consistent with the result of Teodorescu and Matyjaszewski for the attempted ATRP of (meth)acrylamide using this ligand.[22] The screening experiment therefore suggests that bpy should be the ligand of choice among those tested from the point of view of the deactivation rate.

2. ATRP Results. Following the result of the screening test, we attempted ATRP of acrylamide using bpy complexes of CuCl or CuBr as catalysts. As has been mentioned in the Introduction, Wirth et al. polymerized acrylamide (1.75 M) in DMF at 130 °C using benzyl chloride initiator (0.01 M) and bpy ligand and obtained PAM with very narrow MWD (PDI = 1.11).[25] Although the yield was not mentioned in their paper, we calculate it to be 24% in 24 h based on the reported molecular weight assuming that the molecular weight is proportional to conversion as it should be for ATRP. We, on the other hand, found that under the above experimental conditions the polymer precipitates out, the yield is 9% in 24 h, and the MWD is bimodal (PDI = 2.27).

We therefore conducted the polymerization in homogeneous conditions. Since PAM is soluble in water, ethylene glycol, and glycerol among a few others, we used water and glycerol−water mixture (1:1 v/v) as media for polymerization.

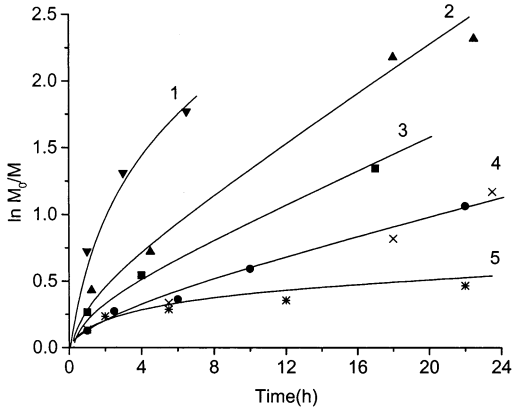


Figure 2. ln M_0/M vs t plots of ATRP of acrylamide for Cl-based initiating systems at 130 °C. Curves 1 to 4 are for ATRP in glycerol−water (1:1 v/v) medium. [Acrylamide] = 4.22 M, [2-Cl-PA] = [CuCl] = 0.008 M; [Cu(I) + Cu(II)]: [bpy] = 1:2. Curves: (1) no additive; (2) in the presence of 0.0016 M $CuCl_2$; (3) in the presence of 1 M LiCl; (4) in the presence of 0.0016 M $CuCl_2$ and 1 M LiCl, (×, repeat experiments); (5) in water in the presence of 0.0016 M $CuCl_2$ and 1 M LiCl.

Table 1. Results of ATRP of Acrylamide at 130 °C for Cl-Based Initiating Systems ([Acrylamide] = 4.22 M, [2-Cl-PA] = [CuCl] = 0.008 M, [Cu(I) + Cu(II)]:bpy = 1:2)

	in presence of		time	%			
set	LiCl (M)	$CuCl_2$:CuCl	(h)	conv	M_n[a]	M_{theo}	PDI
1[b]	0	0	1	51	25 900	19 300	2.2
			3	73	37 800	27 300	2.1
			6.5	83	41 500	31 100	2
2[b]	0	0.2	1.25	35	16 500	13 120	1.85
			4.5	51	21 200	19 270	1.91
			18	88	30 300	33 260	1.81
			22.5	90		33 820	
3[b]	1	0	1.0	23	15 700	8 760	1.85
			4.0	42	21 600	15 750	1.84
			17.0	74	30 400	27 750	1.90
4[b]	1	0.2	1	13		4 900	1.7
			2.5	24	10 700	9 000	1.65
			6.0	30	11 400	11 360	1.68
			10.0	45	16 200	16 800	1.71
			22	65	23 300	24 490	1.7
5[c]	1	0.2	2	21	12 800	7 900	1.7
			5.5	25	13 700	9 400	1.7
			12	30	15 700	11 300	1.6
			22	38	16 200	14 100	1.7

[a] From M_w determined by viscometry and using GPC determined PDI (see Experimental Section). [b] In glycerol−water (1:1 v/v) medium. [c] In water.

2.1. The CuCl-bpy/2-Cl-PA Catalyst Initiator System in Glycerol−Water. The polymerization proceeded homogeneously, and it was reasonably controlled at 130 °C under certain experimental conditions described below. Four sets of experimental conditions were used. In the first set no additive was used. In the second set $CuCl_2$ was added to the reaction mixture to the extent of 20 mol % of CuCl. In the third set $CuCl_2$ was omitted; instead, LiCl was added to a concentration of 1 M. In the fourth set both $CuCl_2$ (20 mol % of CuCl) and LiCl (1 M)[35] were added. A mole ratio of [Cu(I) + Cu(II)]:bpy = 1:2 was used. The results are presented in Figure 2 and Table 1. The ln M_0/M vs t plots shown in Figure 2 reveal that the plots are curved to start with and become linear after certain extents of conversion depending on the additive used. Thus, the linear region extends down to 25% conversion when both $CuCl_2$ and

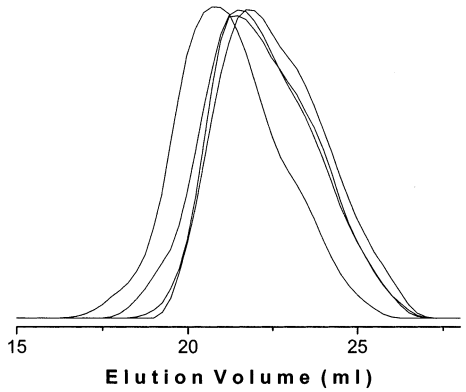


Figure 3. Evolution of GPC traces of PAM prepared in glycerol−water medium at 130 °C under experimental conditions given for set 4 in Table 1.

LiCl were added and to about 40% conversion when $CuCl_2$ or LiCl was added. On the other hand, in set 1, which contained no additive, the curved region extends to at least 70% conversion. In the curved region both termination and deactivation operate, while in the linear region termination is negligible. In keeping with this pattern the molecular weight approaches the theoretical value as conversion increases since the proportion of dead chains decreases as the conversion goes forward in the linear region of the ln M_0/M vs t plot. Also, the agreement of molecular weight with the theoretical value is best for the system which contained both $CuCl_2$ and LiCl and not so good for the one which contained none. In view of the termination reaction which is not negligible in the curved regions of the ln M_0/M vs t plots a close agreement of the experimental $\bar{M}_n$ with the theory is unlikely to obtain. However, some of the initiator lost through termination is replenished by thermally generated radicals deactivated by $CuCl_2$ complex particularly since the polymerization temperature is high, 130 °C.[36,37] A control experiment for set 2 in which all the ingredients except the initiator were present showed that the thermal initiation gave 11% conversion in the first hour compared to 31% for the initiated system (set 2). The thermal contribution however should decrease rapidly with the decrease in monomer concentration since the R_i (thermal) is proportional to the square of the monomer concentration.[38]

The polymerization rate decreases when either $CuCl_2$ and/or LiCl were added to the system, the decrease being largest when both $CuCl_2$ and LiCl were added. In tune with the degree of agreement of molecular weight with the theoretical values the PDI is lowest (1.65−1.7) when both LiCl and $CuCl_2$ were added (set 4) and highest (2−2.2) when none was added (set 1). These results thus suggest that the polymerization is best controlled when both LiCl and $CuCl_2$ are added.

For many ATRP systems use of CuX_2 along with CuX is reported to achieve better control on polymerization, including a linear ln M_0/M vs t plot.[39,40] The effect has been explained as follows. Bimolecular termination of polymer radicals predominates in the initial stages before enough Cu(II) is formed. Extraneous addition of Cu(II) at the start removes this problem. As regards the effect of LiCl, it has been discussed in the Discussion section.

The evolution of GPC traces shown in Figure 3 for set 4 is consistent with the increase in molecular weight with the time of polymerization. However, the traces reveal shoulders in the lower molecular weight side.

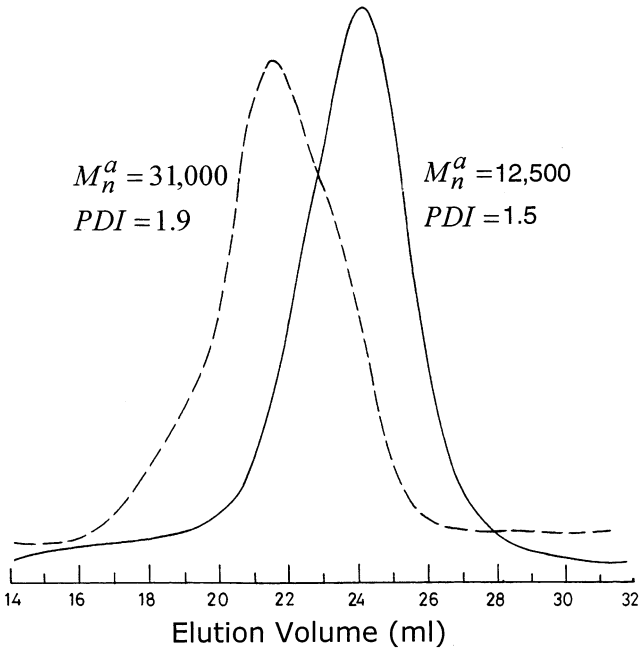


Figure 4. GPC traces for chain extension experiment by two-stage monomer addition. Full curve corresponds to first stage of monomer addition, and the dotted curve corresponds to the second stage of monomer addition.

This result has been dealt with later in this paper in the Discussion section.

Polymerization was also conducted at a lower temperature, viz. 120 °C, using both $CuCl_2$ and LiCl additives and the same recipe as set 4 in Table 1. The ln M_0/M vs t plot was linear down to about 20% conversion (not shown). The conversion reached 40% in 28 h compared to 65% in 22 h at 130 °C. The initiator efficiency was 0.79 and the PDI = 1.7, the latter being the same as was obtained at 130 °C. Thus, the degree of control is almost the same as at 130 °C, but the yield is lower.

2.2. Chain Extension Experiment. Figure 4 shows the GPC traces of the polymer produced in a two-stage monomer addition experiment performed in a glycerol−water medium at 130 °C using both $CuCl_2$ and LiCl additives. In the first stage polymerization was conducted using 4.22 M acrylamide, [CuCl] = [2-Cl-PA] = 0.02 M, [LiCl] = 1 M, [$CuCl_2$] = 0.004 M. After a 25 h reaction period a 71% conversion was reached. In the second stage, monomer concentration was 2.84 M and the conversion was 68%.

The $\bar{M}_n$ and PDI values for the two stages are (1) for the first stage $\bar{M}_n$ = 12 500 (M_{theo} = 10 650), PDI = 1.5 and (2) for the second stage $\bar{M}_n$ = 31 000 (M_{theo} = 26 000), PDI = 1.9. Figure 4 shows that the GPC trace is laterally shifted to the high molecular weight side on going from stage 1 to stage 2. This indicates that the polymers are living. However, the polymer produced in the second stage has a higher PDI due to a tailing in the higher molecular weight side and a shoulder in the low molecular weight side of the GPC trace. The larger PDI may suggest that not all chains are active. It may be noted here that the PDI of the first stage polymer is lower than those reported in Table 1 (set 4). The shoulder in the GPC trace is also not prominent. This improvement in PDI may be a result of using higher (2.5 times as large) concentrations of $CuCl_2$ and CuCl. Broadening of MWD in the second stage of polymerization was also found in the chain extension experi-

Table 2. Results of ATRP of Acrylamide in Glycerol−Water Medium at 130 °C for Br-Based Initiating Systems ([Acrylamide] = 4.22 M, [2-Br-PA] = [CuBr] = 0.008 M, [Cu(I) + Cu(II)]:bpy = 1:2)

	in presence of		time	%			
set	KBr (M)	$CuBr_2$:CuBr	(h)	conv	M_n[a]	M_{theo}	PDI
1	0	0	1	18	9 700	6 750	2.4[b]
			4	25	19 400	9 400	2.3[b]
			9	36		13 400	
			22	60	38 400	22 500	1.9[b]
2	0	0.2	2.33	14		5 440	
			5.5	22	15 500	8 170	1.8
			18.5	51	27 400	19 240	2
			29	60	32 400	22 390	1.8
3	1	0.2	3.66	15	8 100	5 620	2
			13.66	26	12 000	9 750	1.9
			24.75	36	17 200	13 390	1.6

[a] From M_w determined by viscometry and using GPC determined PDI (see Experimental Section). [b] Bimodal distribution.

ments for the ruthenium-based ATRP of *N*,*N*-dimethylacrylamide.[25]

2.3. The CuCl/bpy/2-Cl-PA Catalyst Initiator System in Water. ATRP was also conducted in water under the best conditions established for the glycerol−water medium, i.e., adding both $CuCl_2$ and LiCl. The results at 130 °C are shown in Table 1 (set 5) and Figure 2 (curve 5). It turns out from comparing curve 5 with 4 (glycerol−water medium) that although the linear regions of the curves extend down to about 25% conversion, in both cases the slope of the linear region ($k_p[\dot{M}]$) for the water medium is $^1/_4$ that for the glycerol−water medium. Assuming that k_p for the two media has the same value, $[\dot{M}]$ in water is $^1/_4[\dot{M}]$ in glycerol−water in the nonterminated zone. This result indicates that more Cu(II) formed (more polymer radicals terminated) in the curved zone of the figure in water than in the glycerol−water medium. The molecular weight approaches the theoretical value as conversion increases. On the other hand, the PDI is of the same level as in the glycerol−water system. Nevertheless, the sluggish polymerization in the aqueous medium should rate it inferior to the glycerol−water medium.

Polymerization was also conducted at a lower temperature, viz. 90 °C, using only the LiCl additive. However, the yield was only 5% in 2 h and 10% in 17 h. The molecular weight was about 10 times the theoretical value although the PDI was 1.8. The molecular weight results suggest that the polymerization becomes uncontrolled at 90 °C. Thus, higher temperature improves control.

2.4. The CuBr/bpy/2-Br-PA Catalyst Initiator System in Glycerol−Water. ATRP was also conducted in a glycerol−water medium at 130 °C using CuBr/bpy catalyst and 2-Br-PA initiator with or without the extraneous addition of $CuBr_2$ or both $CuBr_2$ and KBr or LiBr. The results are presented in Table 2 and Figure 5. Polymerization rates are, in general, lower than those of the corresponding Cl-based initiating systems. Figure 5 shows that the ln M_0/M vs t plots are of the same type as obtained with the Cl-based initiating system, and the polymerization rate decreases with the addition of $CuBr_2$ and more greatly with the addition of both $CuBr_2$ and KBr or LiBr. The result is independent of the cation Li or K of the alkali halide. Also, as before, the molecular weight shows better agreement with the theoretical values for systems where both $CuBr_2$ and KBr are added compared to the system where only $CuBr_2$ or none is added. The PDI is also the highest in the latter case.

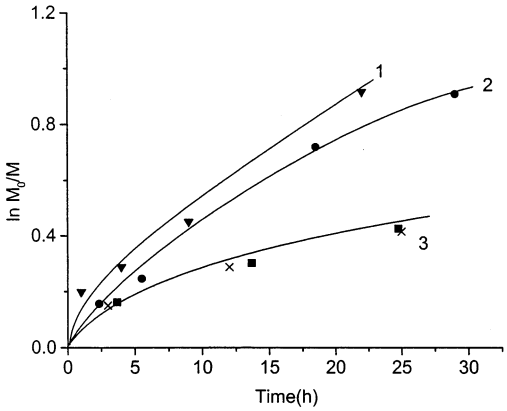


Figure 5. ln M_0/M vs t plots for ATRP of acrylamide in glycerol−water (1:1 v/v) medium at 130 °C for Br-based initiating systems. [Acrylamide] = 4.22 M, [2-Br-PA] = [CuBr] = 0.008 M, [Cu(I) + Cu(II)]: [bpy] = 1:2, curve (1) no additive; (2) in the presence of 0.0016 M $CuBr_2$; (3) in the presence of 0.0016 M $CuBr_2$ and 1 M alkali bromide (×, LiBr; ■, KBr).

The PDI value of 1.6 obtained for set 3 at 36% conversion indicates that the control is almost as good as with the corresponding Cl-based initiating system.

Discussion

Three notable features of ATRP of acrylamide emerge from the present work: (1) controlled polymerization occurs at higher temperature ca. 130 °C. (2) Homogeneous polymerization in glycerol water medium gives better yield than in water medium. (3) Use of extraneously added Cu(II) and/or halide ions improves control on polymerization.

Although the ln M_0/M vs t plot is nonlinear, the shape of the curve suggests that the radical concentration is high to start with which decreases to a steady value after certain extents of polymerization. The high concentration of radicals formed at the start of the reaction allows some bimolecular termination of radicals. This increases the concentration of Cu(II) and decreases that of the chain radical ($\dot{M}$).[40] After the polymerization proceeds for a certain period the concentrations of Cu(II) and of $\dot{M}$ reach a certain level where termination becomes insignificant (persistent radical effect).[41] This situation prevails in the linear region of the ln M_0/M vs t plots where controlled polymerization occurs.

We now examine whether the improved control at increased temperature as observed in aqueous medium is due to any significant increase of k_{deact} over that of k_t. From the work of Dainton et al., $E_{deact} = 22.7 \pm 5.5$ kJ/ mol for termination of polyacrylamide radicals by $Cu^{2+}(H_2O)_4$.[42] As regards E_t, Gromov et al. determined a value of 11.76 ± 0.84 kJ/ mol in water.[43] From these data it may be calculated that k_{deact} will increase 1.4 times faster than k_t for an increase of temperature from 90 to 130 °C. This relative increase may not be large enough to make the higher temperature very suitable. However, the deactivator in the present case is not the aquated Cu^{2+} ion but Cu(II)XL (vide eq 1). E_{deact} for the latter may be different than that for the former and also the composition of the complex (and with it E_{deact}) may change with temperature, so that the estimate given above may not be correct.

As regards the beneficial effect of the added halide ion, we put forward the following explanation. The reaction between a free radical and a transition metal complex may proceed through two pathways: (i) elec-

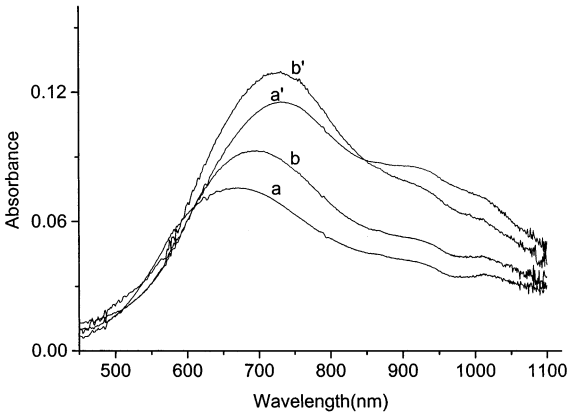
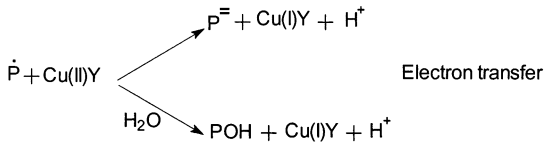


Figure 6. Absorption spectra of bpy complexes of $CuCl_2$ and $CuBr_2$ in water; pH = 8.5, $[CuX_2] = 0.016$ M, [bpy] = 0.032 M, [acrylamide] = 4.22 M. Curves: a and a′ for $CuCl_2$ without and with 1 M LiCl, respectively; b and b′ for $CuBr_2$ without and with 1 M KBr, respectively, at room temperature.

tron transfer and (ii) ligand transfer.[44] The former involves transfer of an electron from the radical to the metal ion. The resulting carbenium ion may either undergo proton elimination and/or substitution reaction with the solvent as shown below for the Cu(II) complex



where Y is a nontransferable ligand; $P^{=}$ and POH represent a polymer molecule with unsaturation and hydroxyl group, respectively, at the polymer chain end.

On the other hand, ligand transfer involves a direct transfer of a ligand from the metal complex to the free radical.

$$\dot{P} + Cu(II)X_m \rightarrow P{-}X + Cu(I)X_{m-1} \quad \text{ligand transfer}$$

Ligands such as H_2O, $RCOO^-$, OH^-, acetylacetonate, pyridine, phenanthroline, bpy, and acetonitrile do not participate in ligand transfer oxidation of radicals. On the other hand, chloride, bromide, thiocyanate, cyanide, and azide ligands do so. For the ATRP to be successful the deactivation reaction should follow the ligand transfer route since the end group formed following the electron transfer process will not be capable of continuing the activation process in ATRP. This means that there should occur no aquation of the Cu(II) complexes in the medium which may not be entirely excluded in an aqueous medium, particularly for Cu(II) complexes with bpy or *o*-phenanthroline.[45] It is also well established that polyacrylamide radicals do undergo termination reaction with $Cu^{2+}(H_2O)_n$ and various aquo and hydroxo species of Fe(III).[46] As mentioned above, these ligands are not involved in ligand transfer reaction.

It is therefore desirable that aquation of Cu(II) complexes by way of replacing halide ion ligands with H_2O is prevented. This is best done by adding halide ions extraneously. Attention to this aspect of the problem of carrying out ATRP in aqueous media was earlier drawn by one of us.[47] Figure 6 shows that the absorption band of the CuX_2/bpy complex undergoes a red shift, and also the intensity of absorption is strongly increased by the addition of halide ions. This supports the view that the halide ion also gets involved in the complex formation. In our view, the better control in the ATRP for the system containing excess halide ion (Table 1, set 4; Table 2, set 3) is achieved through the minimization of aquation of the Cu(II) complexes. The decreased rates of polymerization in systems where halide ions are extraneously added does indeed indicate that the rate of deactivation increases under such conditions. The excess halide ions may also help in having halide ions as ligands in the Cu(I) complexes as well, and this should help in boosting the activation process.

The lower concentration of chain radicals in the termination free region for the water medium compared to the glycerol−water medium under identical experimental conditions (compare set 4 with set 5 in Table 1) may be due to a lower rate of bimolecular termination in the latter medium occurring in the curved region of the ln M_0/M vs t plot. The termination reaction being diffusion-controlled k_t should be lower in glycerol−water medium due to its higher viscosity.[48] In fact, Gromov et al. found that k_t for polyacrylamide radicals decreases with increase in viscosity of medium.[43]

The rather high polydispersity (PDI >1.5) for the present ATRP processes suggests several possibilities:[49,50] (1) initiation may be slower than propagation, (2) k_{act} and k_{deact} are not fast enough, (3) dead polymer chains are present, and (4) there may be involved more than one metal complex for Cu(I) and/or Cu(II). Previous studies of Teodorescu and Matyjaszewski suggested slow activation for ATRP of (meth)acrylamide as has been discussed earlier in this paper.[22] Also, the occurrence of shoulders in the GPC traces may be due to the fact that there exist more than one Cu complexes of either Cu(I) or Cu(II) which do not undergo exchange between themselves at a fast enough rate so as to become an effectively single kinetically important species.

To conclude, this study shows that reasonably controlled ATRP of acrylamide is achieved in glycerol−water medium at 130 °C using both Cl- and Br-based initiating systems in the presence of extraneously added CuX_2 and alkali halides. Replacement of glycerol−water with water results in sluggish polymerization, leading to lower yields.

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