Homogeneous Atom Transfer Radical Polymerization of Methyl Methacrylate at Ambient Temperature in Aqueous Ethanol

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Introduction

The ATRP of several hydrophilic methacrylates at ambient temperature has been reported with moderate to good control in aqueous alcoholic media.[1−12] The control becomes better with increasing alcohol concentration. This has been attributed to (i) the lower rate of polymerization at higher alcohol concentration and (ii) the reduction of the deactivator concentration due to the displacement of the halide ligand from the cupric complexes by water (aquation) or by hydroxyl ion (hydrolysis), which is less at higher alcohol concentration.[10] It is desirable to synthesize controlled hydrophobic polymers as well in such environment-friendly solvents. Recently, the hydrophobic polymer poly(*n*-butyl methacrylate) has been synthesized by ATRP in aqueous isopropanol (i-PA).[13] Surprisingly, the polymerization is not controlled in pure iPA but becomes controlled with significant increase in rate when a small amount of water ca. 7.5% (v/v) was added to i-PA, the polymer remaining soluble in this composition of aqueous i-PA.[13] Poly(methyl methacrylate) (PMMA) is an important hydrophobic polymer soluble in aqueous ethanol[14] (a case of cosolvency). We found the solubility window at 30 °C to exist at $6 \leq$ water $\leq 30\%$ (v/v) for PMMA of $M_n = 20\,000$.

We report herein the successful ATRP of MMA in the environment-friendly solvent aqueous ethanol at ambient temperature. Earlier, we discussed the problems that are encountered with ATRP conducted in media containing water while studying ATRP of acrylamide in aqueous glycerol.[15,16] In this work we have discussed how those problems affect the ATRP of MMA vis-à-vis acrylamide.

Experimental Section

Materials. MMA (BDH) was washed with 5% NaOH solution followed by distilled water, dried over $CaCl_2$, and distilled under reduced pressure. It was stored under a nitrogen atmosphere at −15 °C. CuBr (98%, Aldrich) and CuCl (98%, BDH) were purified by washing with corresponding acids (10% HCl or HBr in water) followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere.[15] Absolute ethanol (Bengal Chemical and Pharmaceutical works, India) was refluxed for 2 h with magnesium wire and distilled. Commercial distilled water was redistilled over alkaline permanganate. *o*-Phenanthroline (*o*-phen, 99.5%, E Merck), bipyridine (bpy, 99+%), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 98%), and ethyl 2-bromoisobutyrate (EBiB, 97%) (all Aldrich products) were used as received.

Polymerization. A typical ATRP synthesis of PMMA is as follows. In a nitrogen-purged reaction vessel (15 mL) provided with a B-19 standard joint were taken CuBr (10 mg, 0.14 mmol) and *o*-phen (54 mg, 0.28 mmol). Deoxygenated (nitrogen-purged) ethanol (2.5 mL), water (0.5 mL), and MMA (3.0 mL, 28 mmol) were next added into the vessel under nitrogen. The vessel was then closed with a rubber septum, which was secured by Cu wire. The admixture was sonicated for 2 min. A deep brown solution was obtained. The vessel was then placed in a thermostated water bath maintained at 35 °C, which is close to room temperature in early summer. Ethyl 2-bromoisobutyrate (EBiB) (20 mg, 0.14 mmol) was next introduced into the vessel using a gastight syringe which was purged with nitrogen. The polymerization was continued for 190 min. The polymerization mixture was then diluted with acetone (3 mL) and poured into excess (30 mL) water−methanol (1:1 v/v). The precipitated polymer was separated by centrifugation, redissolved in acetone, and reprecipitated into water−methanol. The polymer so purified was isolated and dried in a vacuum oven at 45 °C for 48 h and weighed. The yield was 2.28 g (conversion = 80%). NMR data: CH_2 ($\delta = 1.81, 1.9, 1.94, 1.96$, 2H); α CH_3 ($\delta = 0.85, 1.02$, 3 H); CH_3-(ester) ($\delta = 3.6$, 3H). The M_n and PDI of the obtained polymer were 16 000 and 1.15, respectively.

For kinetic study aliquots (1 mL) were withdrawn from time to time from the reaction vessel using gastight syringes and poured into 20 mL of water−methanol. The polymer was isolated and dried as above.

The molecular weights and the molecular weight distributions were measured by GPC at room temperature using a Waters model 510 HPLC pump, a Waters series R-400 differential refractometer, and three Waters Ultrastyragel columns of 10 000, 1000, and 500 Å pore size. HPLC grade THF (Spectrochem, India) was used as the eluent at a flow rate of 1 mL/min. Before injection into the GPC system the polymer solutions were treated with cation-exchange resin Dowex 50 W (Fluka) to free them from Cu salts. They were then filtered through a prefilter−filter combination system compatible with organic solvents. Poly(methyl methacrylate) standards (Waters) were used for calibration. Nuclear magnetic resonance (NMR) spectra were recorded on a 300 MHz Bruker spectrometer using 2% solution of the polymer in $CDCl_3$ at room temperature and tetramethylsilane (TMS) as reference.

Results and Discussion

Entries 1−3 in Table 1 show that the control is good with *o*-phen as the ligand. The polymerization rate increases with increased amounts of water in the medium, as was found for the ATRP of hydrophilic methacrylates.[1−12,17] The higher the rate is, the greater the PDI is. For the other ligands the polymerization was conducted at around the middle of the miscibility window (ethanol:water = 5:1 v/v) where the solvency is expected to be the best.[18] Entry 4 shows that bpy is also an effective ligand. However, it is not as good as *o*-phen is (see later). The PDI values for entries 5 and 6 show that the control is poor with both PMDETA and HMTETA ligands. The former gives incomplete polymerization as well. The result with PMDETA is attributable to considerable disproportionation of the Cu(I)−PMDETA complex as evidenced from the appearance of a blue color which deepens immediately after the addition of the initiator (I). This phenomenon is different from the one that occurs with the use of acrylamide monomer which stabilizes the Cu(I) vs Cu(II) oxidation state through π-complex formation with the former and thus prevents disproportionation.[16] The importance of monomer complexation in preventing Cu(I) disproportionation in some aqueous-based ATRP has been recently discussed by Tsarevsky et al.[12] With the HMTETA ligand disproportionation is less, but the Cu(I)

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Table 1. Results of ATRP of MMA in Ethanol–Water Medium at 35 °C ([MMA] = 3.0 mL (28 mmol), [Ethyl 2-Bromoisobutyrate] = [CuX] = 0.5[Ligand] = 0.14 mmol)

	solvent (mL)							
entry no.	EtOH	H_2O	ligand[a]	time (h)	% conversion	$M_{n,theo}$	$M_{n,GPC}$	M_w/M_n
				CuBr Catalyst				
1	3	0	*o*-phen	5.5	74	14 800	15 200	1.12
2	2.5	0.5	*o*-phen	3.16	80	16 000	16 000	1.15
3	2	1	*o*-phen	3	92	18 400	22 500	1.2
4	2.5	0.5	bpy	2.75	75.5	15 100	15 800	1.2
5	2.5	0.5	PMDETA	18.5	31	6 000	9 000	1.48
6	2.5	0.5	HMTETA	4	90	18 000	21 000	1.64
				CuCl Catalyst				
7	3	0	*o*-phen	9.5	48.5	9 700	8 200	1.22
8	2.5	0.5	*o*-phen	8.33	70	14 000	13 200	1.21

[a] *o*-phen = *o*-phenanthroline, bpy = bipyridine, PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine, and HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine.

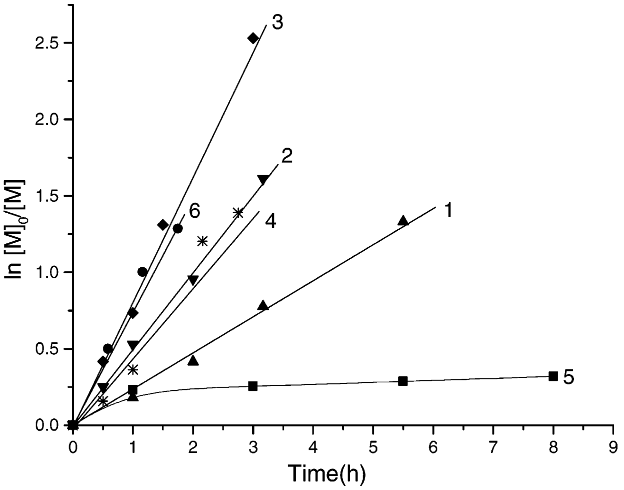

Figure 1. Kinetic plots for the ATRP of MMA in ethanol–water medium at 35 °C. [MMA] = 3.0 mL (28 mmol), [ethyl 2-bromoisobutyrate] = [CuBr] = 0.5[ligand] = 0.14 mmol. Ligand and solvent systems are for curves: 1, *o*-phen and ethanol; 2, *o*-phen and ethanol:water (5:1); 3, *o*-phen and ethanol:water (2:1); 4, bpy and ethanol:water (5:1); 5, PMDETA and ethanol:water (5:1); 6, HMTETA and ethanol:water (5:1) (*o*-phen = *o*-phenanthroline, bpy = bipyridine, PMDETA = *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine and HMTETA = 1,1,4,7,10,10-hexamethyltriethylenetetramine).

complex immediately oxidizes on addition of the initiator, giving rise to a deep blue color; but the Cu(II) complex turns out to be a poor deactivator, giving rise to polymer of higher PDI.

The kinetic plots for the first-order disappearance of the monomer (M) as shown in Figure 1 are linear except when PMDETA was used as the ligand. This result suggests that termination is negligible compared to deactivation except with PMDETA.[19] Figures 2 and 3 respectively show the variation of M_n and PDI with conversion using *o*-phen or bpy ligands. With the *o*-phen ligand M_n increases linearly with conversion particularly in ethanol or in ethanol:water = 5:1, indicating good livingness of the systems. On the other hand, with the bpy ligand the variation of M_n with conversion is nonlinear. M_n agrees with the theoretical values only at high conversion, ca. 70% and above.[20] Thus, termination is more when bpy is the ligand than when *o*-phen is. The PDI is low (≤1.3) and decreases with conversion using the *o*-phen ligand. This is in agreement with the theoretical prediction.[21–23] On the other hand, with bpy it increases with conversion after an initial decrease. Also, the PDI values for the two low-conversion polymers, viz. 14 and 30%, are surprisingly low, being 1.18 and 1.16, respectively, although as Figure 2 shows, the M_ns for these two conversions are much greater than the theoretical values. An explanation of this anomaly is not immediately apparent.

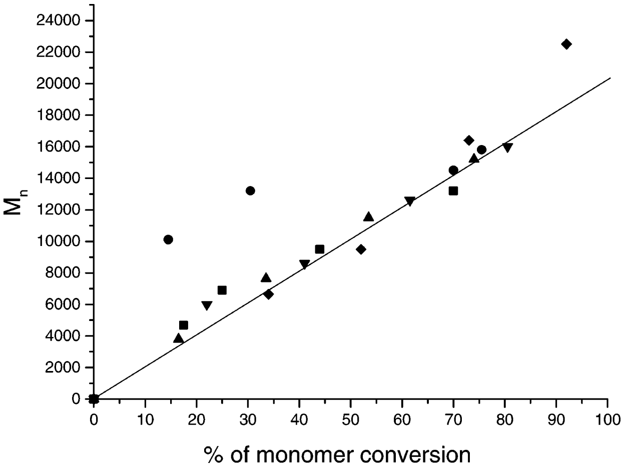

Figure 2. Evolution of M_n with conversion in the ATRP of MMA at 35 °C using CuBr/L and CuCl/L catalysts. [MMA] = 3.0 mL (28 mmol), [ethyl 2-bromoisobutyrate] = [CuX] = 0.5[ligand] = 0.14 mmol. Systems: (▲) ethanol, *o*-phenanthroline, and CuBr; (▼) ethanol:water (5:1), *o*-phenanthroline, and CuBr; (◆) ethanol:water (2:1), *o*-phenanthroline, and CuBr; (●) ethanol:water (5:1), bipyridine, and CuBr; (■) ethanol:water (5:1), *o*-phenanthroline, and CuCl; (—) theoretical line.

Earlier, Matyjaszewski et al. established that the mixed halide initiation system EBiB/CuCl gives much better control in the ATRP of MMA in nonaqueous medium (diphenyl ether) using 4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) as the ligand.[24] This was attributed to faster initiation due to the weaker C–X bond in the initiator when X = Br and slower propagation due to the polymer chain end predominantly (ca. 90%) containing the stronger C–Cl bond. Besides, the C–Br bond at the polymer chain end undergoes undesired side reactions.[24]

In contrast, the present work shows that in pure or aqueous ethanol better control is achieved with the EBiB/CuBr initiation system than with the mixed halide initiation system EBiB/CuCl. This is substantiated from an examination of the PDI values obtained with these two initiation systems both in ethanol and in ethanol:water (5:1), as shown in Figure 3. The PDI curves for the EBiB/CuCl lie above those for the EBiB/CuBr initiation system both in ethanol (curve 2 vs 1) and in ethanol:water (curve 4 vs 3). This result may be attributed to the greater loss of the deactivator CuX_2/L

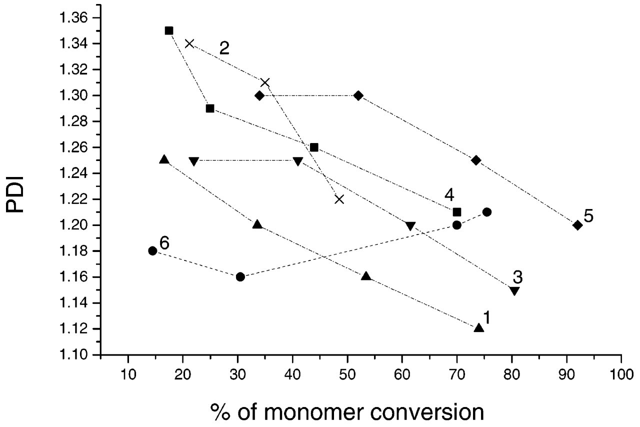

Figure 3. Evolution of PDI with conversion in the ATRP of MMA at 35 °C using CuBr/L and CuCl/L catalysts. [MMA] = 3.0 mL (28 mmol), [ethyl 2-bromoisobutyrate] = [CuX] = 0.5[ligand] = 0.14 mmol. Systems: (▲) ethanol, *o*-phenanthroline, and CuBr; (×) ethanol, *o*-phenanthroline, and CuCl; (▼) ethanol:water (5:1), *o*-phenanthroline, and CuBr; (■) ethanol:water (5:1), *o*-phenanthroline, and CuCl; (◆) ethanol:water (2:1), *o*-phenanthroline, and CuBr; (●) ethanol:water (5:1), bipyridine, and CuBr.

when X is Cl through the exchange of X^- from the complex with ethanol and/or water. The stability constants data of the CuX_2/L complexes in ethanol are not available in the literature. However, the available stability constants data of CuX^+ and CuX_2 in methanol, $\beta(CuBr^+) = 5200$, $\beta(CuCl^+) = 280$, $\beta(CuBr_2) = 390\,000$, $\beta(CuCl_2) = 16\,000$ at 25 °C,[25] demonstrate that the loss of halide ion from the complexes will be more when X = Cl^-. Also, the deactivator for the mixed halide initiated system is CuClBr/L. The extent of loss of halide ligand from this complex will be intermediate between those for $CuBr_2$/L and $CuCl_2$/L, and thus CuClBr/L should be a poorer deactivator than $CuBr_2$/L in such media. A similar situation should exist in ethanol. Additionally, the $\beta(Cu(H_2O)^{2+})$ value of 0.59 at 20 °C[26] in ethanol suggests that considerable aquation of Cu^{2+} in aqueous ethanol would take place in view of the high water concentration. Recently, Tsarevsky et al. made use of the stability constant data of $CuCl^+$, $CuBr^+$, and $Cu(H_2O)^{2+}$ and calculated that the Cu−X bond will be dissociated in methanol:water (2.3:1 v/v) to the extent of 23% and 66% for X = Br and Cl, respectively.[10] They expected that similar dissociation should take place in the presence of the chelating ligand also.

In general, the loss of the halide ligand affects the ATRP in two ways: (i) it decreases the rate of deactivation due to the decrease of the concentration of CuX_2/L, and (ii) the halide-free solvent ligated Cu^{2+} ions generated in the process may cause oxidative termination of the polymer radicals by an outer-sphere electron-transfer process[27] as has been reported for the reaction of $Cu^{2+}(H_2O)_x$ ions with polyacrylamide radicals.[28] This has been one of the principal reasons why ATRP of acrylamide has been difficult in aqueous-based medium.[15,16] Both of the above two problems can however be overcome by the extraneous addition of both CuX_2 and excess halide ions.[10,15,16] Fortunately, the PMMA radical does not undergo electron-transfer oxidation by aquated Cu^{2+} ions. It does not do so with aquated Fe^{3+} either,[29,30] which was attributed to a steric effect.[30] The problem, therefore, is much less in the ATRP of MMA. This may be true for other methacrylates, too, which could be the reason for ATRP being moderately successful with them without addressing these problems. However, Tsarevsky et al. recently considered the first problem while trying to reduce the higher PDI obtained in the case of the ATRP of 2-hydroxyethyl methacrylate and 2-(*N*,*N*-dimethylamino)ethyl methacrylate in water, methanol, or their mixtures using CuCl/bpy catalyst.[10] The PDI was satisfactorily lowered by the extraneous addition of both $CuCl_2$ and a chloride salt.[10] An identical solution was independently provided by us to solve both the two problems which affect the ATRP of acrylamide.[15,16]

Table 1 also shows that the rate of polymerization is faster with the CuBr/L catalyst system. This result agrees with the previous reports in the literature on the ATRP of MMA in nonaqueous media.[31,32] However, while the R−Br + CuBr/L initiator−catalyst system gives a higher rate of polymerization than the R−Cl + CuCl/L with MMA,[31,32] the opposite is true for acrylamide.[15,16]

Obviously, the equilibrium constant for the reversible deactivation $K = k_a/k_{da}$ (where k_a and k_{da} are the rate constants for the activation and deactivation reactions in ATRP) is greater for a Br-based system in the ATRP of MMA, but the reverse is true in the ATRP of acrylamide.

Matyjaszewski et al. argued that the k_a would be greater for a Br-based system than for a Cl-based one since the C−Br bond at the polymer chain end is weaker than the C−Cl. We believe that consideration should also be given to the fact that k_{da} is greater with $CuBr_2$ than with $CuCl_2$.[33,34] The two effects therefore oppose each other. However, the former effect should be overriding for MMA as explained in the following. Bamford et al. established that the α-methyl group in the penultimate unit of the PMMA radical imposes a considerable steric hindrance in transfer reactions involving large atoms such as Br in CBr_4.[35−37] We expect this steric effect to be operative in Br atom transfer reactions from $CuBr_2$/L as well. Accordingly, the extent of increase of k_{da} due to the replacement of $CuCl_2$ by $CuBr_2$ would be much less than what would the bond strengths and the substrate polarity dictate. Because of the absence of any α-substituent in acrylamide, the steric effect on k_{da} should be absent. Hence, the results are different for the two monomers.

In summary, the ATRP of MMA is facile and well controlled at ambient temperature in the environment-friendly solvent, aqueous ethanol, using the CuX/*o*-phen catalyst system.

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