Preparation of Poly(oligo(ethylene glycol) monomethyl ether methacrylate) by Homogeneous Aqueous AGET ATRP

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ABSTRACT: A new convenient initiation process for ATRP, activators generated by electron transfer (AGET ATRP), was investigated in homogeneous aqueous solution at ambient temperature (30 °C). Tris[(2-pyridyl)-methyl]amine (TPMA)/$CuBr_2$ complex was used as an oxidatively stable Cu(II) precursor. Ascorbic acid was used as a reducing agent to reduce the air-stable Cu(II) complex, resulting in generation of an active catalyst. Two oligo(ethylene glycol) monomethyl ether methacrylates (OEOMA) with different pendent OEO chain lengths (OEOMA300 and OEOMA475) were used to demonstrate the broad applicability of aqueous AGET ATRP for the synthesis of well-controlled water-soluble homopolymers and random copolymers at the targeting degree of polymerization (DP) = 300. Concentrations of Cu(II) complex and ascorbic acid as well as ratio of water to macromonomer were varied to produce well-controlled homopolymers of P(OEOMA300) and P(OEOMA475) as well as random copolymer P(OEOMA300-*ran*-OEOMA474) with DP > 240 and $M_w/M_n < 1.3$. $CuCl_2$/TPMA complex resulted in a slower but better controlled polymerization than $CuBr_2$/TPMA complex. The $CuBr_2$/bpy complex produced polymers with broader molecular weight distribution than the $CuBr_2$/TPMA complex. Aqueous AGET ATRP retains all of the benefits of normal ATRP. Additionally, it provides a facile route for the preparation of polymers due to the use of oxidatively stable catalyst precursors.

Introduction

Atom transfer radical polymerization (ATRP) is one of the most successful controlled/living radical polymerization (CRP) techniques.[1] It enables synthesis of a wide spectrum of polymers with control over molecular weight and narrow molecular weight distribution (i.e., M_w/M_n, or polydispersity, PDI < 1.5).[2] ATRP also allows for the synthesis of copolymers with different chain architectures, such as block, random, gradient, comb-shaped, brush, multiarmed, end-functional, and star copolymers.[3] Generally ATRP is conducted in various homogeneous media such as bulk[4] or organic solvents.[5] ATRP has been also carried out in "green" solvents, including carbon dioxide[6] and ionic liquids,[7] that can be used to replace volatile, potentially toxic organic solvents. Since the first aqueous ATRP was successfully applied to the synthesis of poly(2-hydroxyethyl acrylate),[8] there has been a continuous effort to conduct ATRP of hydrophilic and water-soluble monomers in aqueous media.[9] However, control is limited, and polymers of relatively low molecular weight are typically formed in aqueous ATRP.

Poly(sodium methacrylate),[10] poly(sodium vinylbenzoate) (PNaVBA),[11] poly(2-hydroxyethyl methacrylate),[12] and poly-(oligo(ethylene glycol) monomethyl ether methacrylate) (P(OEOMA))[13−16] were successfully synthesized in aqueous media. However, success was only attained over a limited range of conditions, producing polymers of relatively low molecular weight. For example, the aqueous ATRP of NaVBA using the CuBr/bpy complex was fast and reached 95% conversion within 30 min, at 20 °C. However, the resulting polymers had low molecular weight, with the targeted degree of polymerization (DP) = 100 and a molecular weight distribution of M_w/M_n = 1.32. OEOMA, a methacrylate-based macromonomer with pendent oligo(ethylene oxide) (OEO) chains, is an interesting water-soluble monomer. Several grades of OEOMA with different OEO chain lengths are commercially available, including OEOMA300 (M = 300 g/mol, pendent EO units DP ≈ 7), OEOMA475 (M = 475 g/mol, pendent EO units DP ≈ 9), and OEOMA1100 (M = 1100 g/mol, pendent EO units DP ≈ 23). The ATRP of these macromonomers has been conducted in water at 20 °C using CuBr/bpy[13,14] or CuCl/pyridylmethanimine[15] as the catalyst. Although high conversion was attained, >99% in less than 30 min, the only reactions that were successful targeted a DP in the range of 10−33 at complete conversion, i.e., polymers with relatively low molecular weights. Attempts to synthesize higher molecular weight P(OEOMA), DP = 100, failed, resulting in the synthesis of polymers with bimodal distribution.[13] Recently, relatively high molecular weight P(OEOMA) with targeted DP = 200 at >95% conversion was synthesized using CuBr/bpy in a mixture of MeOH and water (70:30 v/v).[17] There are also many examples of successful ATRP of water-soluble monomers but in nonaqueous media.[18,19]

Aqueous ATRP is generally fast and typically yields polymers with relatively high polydispersity, indicating either poor control or actual loss of control.[16] For example, aqueous ATRP of *N*,*N*-dimethylacrylamide at room temperature was completed in less than 1 min, but no control was achieved.[20] The loss of control may be due to several side reactions in aqueous ATRP.[21] The main side reaction could be hydrolysis of the ATRP deactivator (X-Cu(II)/L_m) in the presence of water. This involves irreversible dissociation of the halide ligand (X) from the higher oxidation state complex to form a stable inactive species (Cu(II)/L_m). Consequently, the concentration of deactivator is decreased, resulting in a reduction of the rate of deactivation, leading to faster polymerization and eventually loss of control. To suppress the dissociation of deactivator and retain control in aqueous ATRP, a sufficient concentration of deactivator in the reaction media is necessary. Several approaches for normal ATRP, including addition of sufficient amount of halide salts and extra Cu(II)−halide complex, and the use of protic solvent as a cosolvent were suggested.[21]

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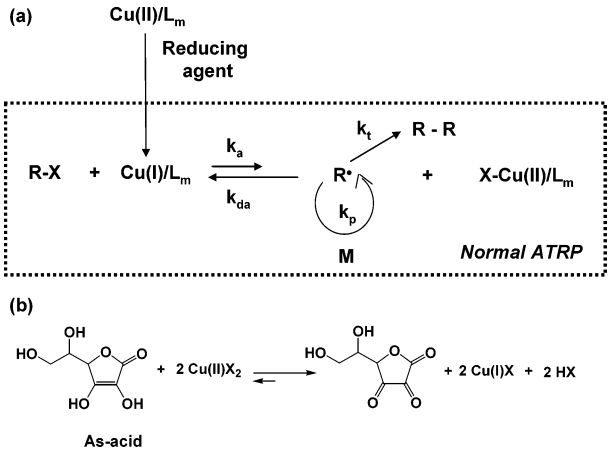
Scheme 1. AGET ATRP Compared with Normal ATRP (a) and Reduction Mechanism of Cu(II)X_2 to Cu(I)X in the Presence of Ascorbic Acid as a Reducing Agent (b)



A new initiating process for ATRP, activators generated by electron transfer (i.e., AGET ATRP), has been recently introduced. In this process, the active Cu(I)/L_m catalyst is formed by the reaction of reducing agents, such as ascorbic acid or tin(II) 2-ethylhexanoate, with an oxidatively stable Cu(II)/L_m precursor prior to normal initiation with the added alkyl halide initiator (R−X). The process then follows normal ATRP where the Cu(I) complex reacts with the dormant species to generate a deactivator X-Cu(II)/L_m and an active radical (R•) (Scheme 1). This process provides all benefits of normal ATRP and the additional advantage that a more stable catalyst complex can be added to the reaction mixture as in reverse ATRP[22] as well as simultaneous reverse and normal initiation (SR&NI) processes.[23] Furthermore, in contrast to the both reverse and SR&NI processes, the AGET process allows for the synthesis of pure block copolymers.[24,25] This new method was successful in polymerization of hydrophobic monomers, such as styrene and nonpolar (meth)acrylates, in bulk[25] as well as in miniemulsion[24] and microemulsion.[26]

In this paper we describe how AGET ATRP can be adapted to aqueous systems by extending the process from hydrophobic to hydrophilic monomers and water-soluble systems. Since only the oxidatively stable Cu(II)/L_n precursor is added to the reaction mixture, this allows improved control over the concentration of Cu(II) complex in the polymerization medium throughout the reaction, resulting in better control. OEOMA300 and OEOMA475 were the monomers used for AGET ATRP targeting DP = 300 in water at ambient temperature (30 °C). This approach was successful for the synthesis of well-controlled, relatively high molecular weight, water-soluble homopolymers and random copolymers of P(OEOMA).

Experimental Section

Materials. OEOMA300 and OEOMA475 were purchased from Aldrich and purified by passing through a column filled with basic alumina to remove inhibitor. Copper(II) bromide ($CuBr_2$, 99%) was used as received from Acros. 2,2′-Bipyridine (bpy, 99+%), 4-(dimethylamino)pyridine (DMAP, 99+%), 1,3-dicyclohexylcarbodiimide (DCC, 99%), and L-ascorbic acid (AscA, 99+%) were used as received from Aldrich. Poly(ethylene glycol) monomethyl ether with M = 5000 (PEO5000-OH) was used as received from Fisher Scientific. Tris[(2-pyridyl)methyl]amine (TPMA) was prepared as described elsewhere.[27] A water-soluble macroinitiator, PEO-functionalized 2-bromoisobutyrate (PEO5000-Br), was synthesized by the reaction of PEO5000-OH with 2-bromo-2-methylpropionic acid (98%, Aldrich) in the presence of DCC and DMAP in chloromethane (CH_2Cl_2), as described elsewhere.[28]

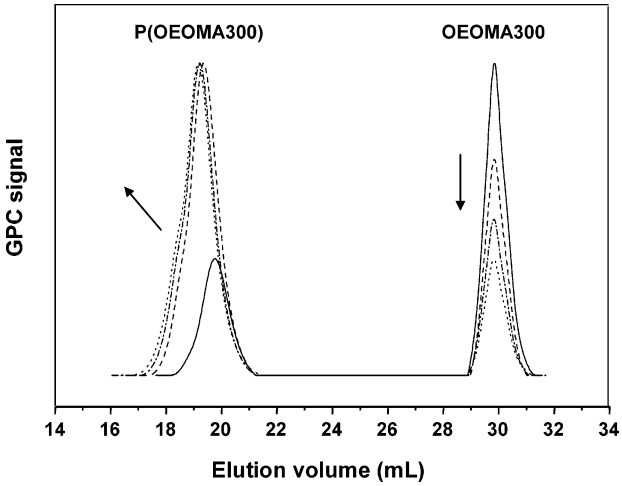


Figure 1. GPC traces of OEOMA300 macromonomer and P(OEOMA300). Conversion of OEOMA300 was calculated by detecting decrease of the monomer peak area. PEO5000-Br macroinitiator and toluene as an internal standard are eluted at 22−24 mM and 33−35 mL, respectively.

General Procedure for AGET ATRP of OEOMA in Water. A series of aqueous AGET ATRP reactions, using OEOMA300 and OEOMA475, were carried out under different experimental conditions at 30 °C. An example detailing a typical procedure for the synthesis of P(OEOMA300) follows: OEOMA300 (4.0 g, 13.3 mmol), PEO5000-Br (228.0 mg, 0.044 mmol), $CuBr_2$ (5.0 mg, 0.022 mmol), TPMA (6.5 mg, 0.022 mmol), and water (15 mL) were added sequentially to a 25 mL Schlenk flask. The resulting transparent solution was deoxygenated by purging with argon for 30 min at room temperature. The flask was immersed in an oil bath preheated to 30 °C. An argon-purged solution of AscA (0.03 mmol/mL, 0.12 mL, 3.3 μmol) was added to the flask in order to reduce the Cu(II) complex to the activator Cu(I) complex and start the polymerization. Samples were withdrawn at different time intervals during the polymerization for GPC measurements to monitor conversion and provide molecular weight data. The polymerization was stopped by exposing the catalyst to air.

For the synthesis of P(OEOMA475), as an example, OEOMA475 (4.0 g, 8.4 mmol), PEO5000-Br (144.0 mg, 0.028 mmol), $CuBr_2$ (3.1 mg, 0.014 mmol), TPMA (4.1 mg, 0.014 mmol), AscA (0.03 mmol/mL, 0.07 mL, 2.1 μmol), and water (10 mL) were used.

A random copolymerization of OEOMA300 and OEOMA475 was conducted by a similar procedure, except that OEOMA300 (2.0 g, 6.7 mmol), OEOMA475 (2.0 g, 4.2 mmol), PEO5000-Br (184.0 mg, 0.036 mmol), $CuBr_2$ (4.0 mg, 0.018 mmol), TPMA (5.3 mg, 0.018 mmol), AscA (0.03 mmol/mL, 0.09 mL, 2.7 μmol), and water (15 mL) were used.

Instrumentation and Analyses. The molecular weights of the P(OEOMA) samples were determined by gel permeation chromatography (GPC). The GPC was conducted with a Waters 515 pump and Waters 410 differential refractometer using PSS columns (Styrogel 10^5, 10^3, 10^2 Å) in THF as an eluent at 35 °C and at a flow rate of 1 mL/min. Linear poly(methyl methacrylate) (PMMA) standards were used for calibration. For GPC measurements, an aliquot of the polymer samples was dissolved in THF, containing a small amount of toluene as internal standard, and then filtered through a column filled with alumina to remove Cu species. The theoretical molecular weights reported in this paper were predicted from the ratio of monomer to initiator ($M_{n,theo}$ = MW(PEO5000-Br) + MW(OEOMA) × ([OEOMA]$_0$/[PEO5000-Br]$_0$) × conversion). Conversion was also determined using GPC by following the decrease of the macromonomer peak area relative to the increase of polymer peak area, as shown in Figure 1.

Results and Discussion

Synthesis of P(OEOMA300). All ingredients were completely soluble in water to form a clear aqueous solution. A

Table 1. Detailed Experimental Conditions and Properties of Final P(OEOMA300) Prepared by AGET ATRP Targeting DP = 300 in Water at 30 °C with a Cu(II)/TPMA Complex[a]

entry	OEOMA300/ PEO5000-Br/ CuX_2-TPMA/AscA	CuX_2	CuX_2 [mM][b]	AscA [mol %][c]	AscA [mM][b]	time [min]	conv	$M_{n,theo}$[d]	$M_{n,GPC}$	M_w/M_n
1	300/1/1/0.3	$CuBr_2$	2.34	30	0.67	40	0.87	85 700	112 000	1.59
2	300/1/1/0.08	$CuBr_2$	2.34	8	0.18	60	0.51	50 600	51 300	1.15
3	300/1/0.5/0.08	$CuBr_2$	1.17	15	0.18	40	0.8	75 600	71 800	1.29
4	300/1/0.5/0.04	$CuBr_2$	1.17	8	0.09	50	0.48	45 500	50 600	1.21
5	300/1/0.25/0.04	$CuBr_2$	0.58	15	0.09	52	0.54	51 100	63 000	1.32
6	300/1/0.5/0.08	$CuCl_2$	1.17	15	0.18	120	0.66	64 700	69 700	1.29
7	300/1/1/0.15	$CuCl_2$	2.34	15	0.35	135	0.78	74 300	87 000	1.26

[a] The ratio of water to OEOMA300 = 3.8/1 v/v. [b] The concentration in water + OEOMA300. [c] Mol % of Cu(II) catalyst. [d] $M_{n,theo}$ = MW (PEO5000-Br) + MW(OEOMA300) × ($[OEOMA300]_0/[PEO5000\text{-}Br]_0$) × conversion.

water-soluble PEO-functionalized 2-bromoisobutyrate (PEO5000-Br) was synthesized to produce PEO-*b*-P(OEOMA) block copolymers. Ascorbic acid was used as the reducing agent. A complex of TPMA with $CuBr_2$ was selected as the stable catalyst precursor for aqueous ATRP in the experiments. The use of TPMA ligand leads to a water-soluble and active complex, with relatively small tendency toward dissociation in water.[29] A series of AGET ATRP of OEOMA300 targeting DP = 300 were conducted in water at ambient temperature under different experimental conditions. Table 1 summarizes the detailed experimental conditions, conversion, and molecular weight data of the final P(OEOMA300) prepared in the presence of Cu(II)/TPMA catalyst complex.

1. Effect of Concentration of Cu(II) and Ascorbic Acid. In an AGET ATRP the added ascorbic acid reduces the oxidatively stable Cu(II)/ligand precursor to the active Cu(I)/ligand complex (Scheme 1). Consequently, the concentration of ascorbic acid and Cu(II) complex added to the reaction mixture directly influences the ratio of Cu(I)/L_m activator to X-Cu(II)/L_m deactivator in the reaction mixture and ultimately the rate of polymerization as well as the molecular weight distribution of the polymer formed in an ATRP.

The following experiments were conducted to examine the effect of varying the concentration of $CuBr_2$/TPMA complex and ascorbic acid on an AGET ATRP of OEOMA300 in water at 30 °C. AGET ATRP of OEOMA300 was first conducted with an initial molar ratio of $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0$ = 300/1/1. Two different concentrations of ascorbic acid were used: $[AscA]_0$ = 0.67 mM (30 mol % of Cu(II), entry 1) and $[AscA]_0$ = 0.18 mM (8 mol % of Cu(II), entry 2). The rate of polymerization increased with [AscA], as shown in Figure 2. This increase is due to the formation of a higher concentration of Cu(I) complex in the presence of more ascorbic acid. For AGET ATRP with higher $[AscA]_0$ = 0.67 mM, polymerization was fast and 87% conversion was reached in 40 min (entry 1, Figure 2). Molecular weight increased with conversion. However, the molecular weight distribution also increased and was relatively broad (M_w/M_n = 1.21−1.60) (Figure 3a). The GPC traces of P(OEOMA300) at conversions higher than 20% show bimodal distribution (Figure 3b). The higher molecular weight species had peak molecular weights twice higher than those of the lower molecular weight species. This could suggest that the high molecular weight species were formed by termination. This could be ascribed to a high concentration of radicals in the reaction mixture, resulting from the high concentration of ascorbic acid added to the reaction mixture. The relative portion of the high molecular weight species increased with conversion. For ATRP of OEOMA300 with low $[AscA]_0$ = 0.18 mM, polymerization reached a plateau at around 50% conversion (entry 2, Figure 2). Molecular weight increased with conversion, and molecular weight distribution was narrow (M_w/M_n = 1.12−1.15). However, bimodal distributions were also observed.

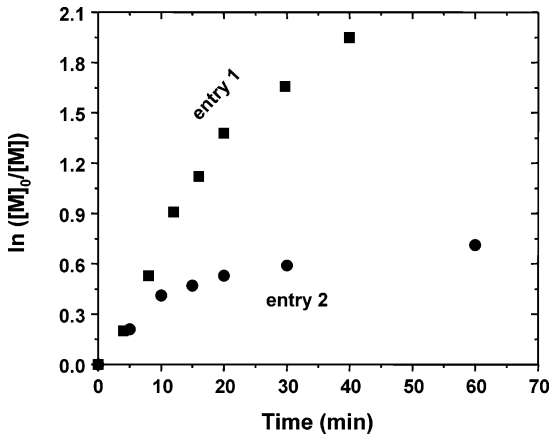


Figure 2. First-order kinetic plots for AGET ATRP of OEOMA300 in water at 30 °C. Conditions: $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0$ = 300/1/1 with the different concentrations of ascorbic acid; [AscA] = 0.67 mM (entry 1) and [AscA] = 0.18 mM (entry 2).

In another set of experiments, the effect of adding smaller amounts of Cu(II) complex and ascorbic acid was examined. Here the molar ratio was $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0$ = 300/1/0.5 with varied concentrations of ascorbic acid; $[AscA]_0$ = 0.18 mM (15 mol % of Cu(II), entry 3) and $[AscA]_0$ = 0.09 mM (8 mol % of Cu(II), entry 4). First-order kinetic plots (Figure 4) show that AGET ATRP reaction with $[AscA]_0$ = 0.09 mM reached a plateau at around 50% conversion. However, AGET ATRP with $[AscA]_0$ = 0.18 mM reached 80% conversion in 40 min. The slight curvature in the first-order kinetic plot could indicate a possible termination. As shown in Figure 5a, molecular weight increased linearly with conversion. The values obtained by GPC with PMMA standards were close to the theoretical values. Molecular weight distribution was narrow, M_w/M_n < 1.3. Figure 5b shows the GPC traces of P(OEOMA300) prepared with 15% ascorbic acid of Cu(II) complex. A slight shoulder was seen in the GPC traces at conversion higher than 70%. These results confirm that relatively high molecular weight P(OEOMA300) was successfully synthesized in water in a controlled fashion. Conversion was over 80%, with narrow molecular weight distribution (DP = 240, M_w/M_n = 1.29).

A further decrease in the amount of $CuBr_2$/TPMA complex was examined with $[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0$ = 1/0.25 and $[AscA]_0$ = 0.09 mM (15 mol % of Cu(II), entry 5). Conversion reached a plateau at around 54%. The value of molecular weight obtained by GPC was 1.3 times as large as the theoretical value; however, the molecular weight distribution was fairly narrow (M_w/M_n = 1.32).

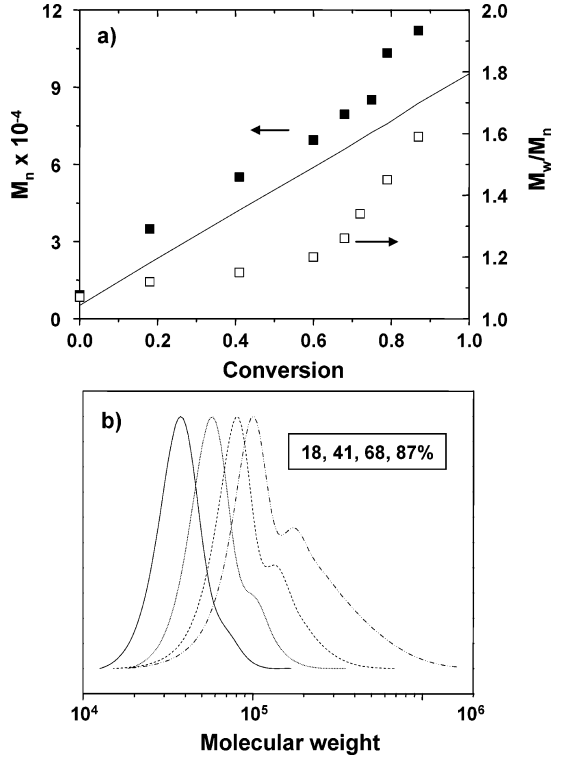


Figure 3. Evolution of molecular weight and molecular weight distribution (a) and GPC traces with conversion (b) for AGET ATRP of OEOMA300 in water at 30 °C. Conditions: $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0 = 300/1/1$ with [AscA] = 0.67 mM (entry 1). The straight line is theoretically calculated molecular weight.

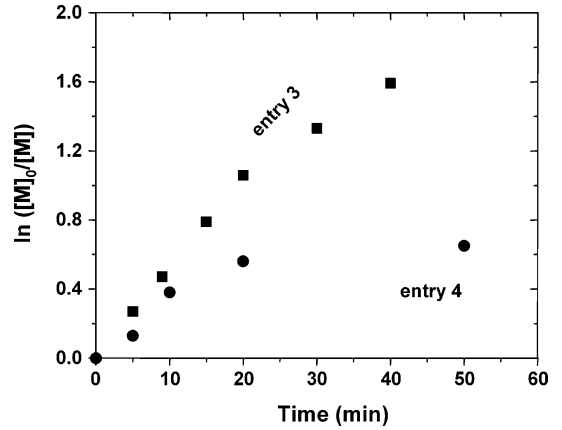


Figure 4. First-order kinetic plots for AGET ATRP of OEOMA300 in water at 30 °C. Conditions: $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0 = 300/1/0.5$ with [AscA] = 0.18 mM (entry 3) and [AscA] = 0.09 mM (entry 4).

2. Effect of Catalyst. A $CuCl_2$ catalyst with TPMA ligand was also examined for AGET ATRP of OEOMA300 in water. Results are shown in Figure 6 and presented in Table 1. The rate of polymerization with $CuCl_2$/TPMA complex was slower than with $CuBr_2$/TPMA complex. For example, it took 90 min to reach 60% conversion (entry 6), as compared to 20 min in the presence of $CuBr_2$/TPMA catalyst (entry 3), under similar experimental conditions. The difference could be due to the stronger C−Cl bond than the C−Br bond.[30] Figure 6a shows that conversion increased with time for AGET ATRP of OEOMA300 in the presence of a $CuCl_2$/TPMA complex (entry 7). Molecular weight increased with conversion, and values obtained by GPC were close to the theoretically calculated ones. Moreover, the molecular weight distribution was low with $M_w/M_n = 1.18-1.26$ (Figure 6b). These results suggest that the level

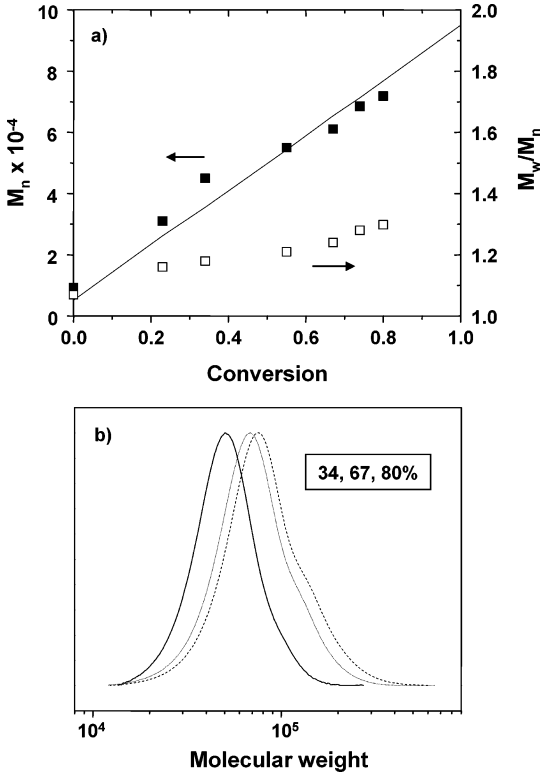


Figure 5. Evolution of molecular weight and molecular weight distribution (a) and GPC traces with conversion (b) for AGET ATRP of OEOMA300 in water at 30 °C. Conditions: $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0 = 300/1/0.5$ with [AscA] = 0.18 mM (entry 3). The straight line is theoretically calculated molecular weight.

of control for AGET ATRP of OEOMA300 in the presence of $CuCl_2$/TPMA was similar to that of the $CuBr_2$/TPMA catalyst (entry 3). However, a higher concentration of the $CuCl_2$ based catalyst was needed (entry 7) to attain similar results. This is plausibly due to the slower reaction and lower radical concentration. Figure 6c shows the monomodal GPC traces of P(OEOMA300).

3. Effect of Ligand. Bpy, a commercially available ligand, forms a water-soluble Cu(II) complex. Compared to TPMA, a bpy-based catalyst is less active but has a similar tendency toward dissociation in water.[29] Bpy was used with both CuBr and CuCl for previously reported aqueous ATRP of P(OEOMA).[13,14] In our experiments, a $CuBr_2$/bpy complex was examined for aqueous AGET ATRP of OEOMA300 starting with $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2]_0/[bpy]_0/[AscA]_0 = 300/1/0.5/1/0.08$. The results are summarized in Table 2. The rate of polymerization was similar to that found for the TPMA ligand. This result confirmed that more active ATRP complexes are reduced to a lesser degree in the presence of the same reducing agents.[25] Consequently, the activity and the reducing effect of the catalyst might compensate for each other and reduce the influence of ligands on the rate of polymerization in AGET ATRP. However, the values of molecular weight were 1.4 times higher than the theoretically predicted values. In addition, the polydispersity at 71% conversion was $M_w/M_n = 1.53$, higher than that obtained using TPMA ($M_w/M_n = 1.29$), indicating poorer control.

Synthesis of P(OEOMA475). AGET ATRP of OEOMA475 was conducted under similar conditions in water at ambient temperature (30 °C). The initial molar ratio of reagents was $[OEOMA475]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0 = 300/1/0.5$ with 15 mol % ascorbic acid of Cu(II). Table 3 presents the results. For AGET ATRP of OEOMA475 (entry 8), conversion

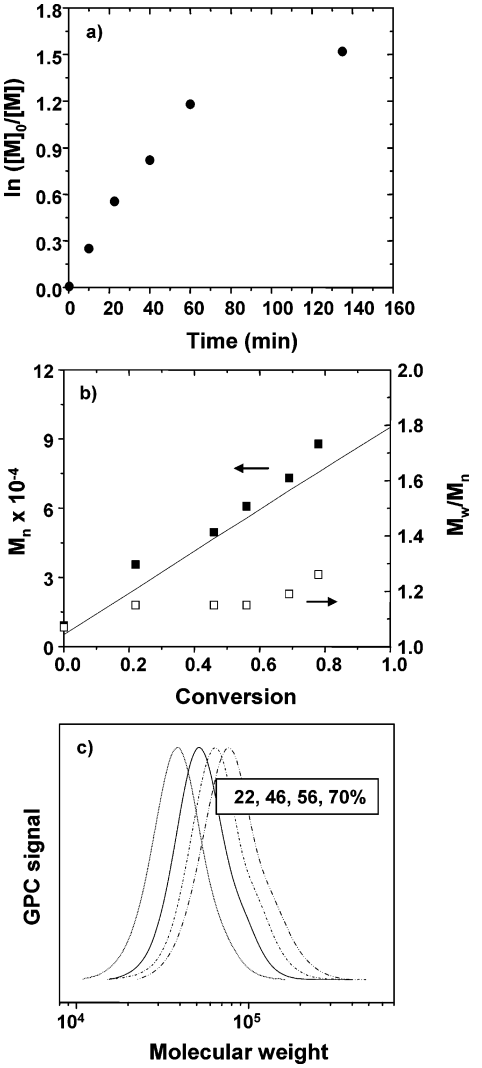


Figure 6. First-order kinetic plot (a), evolution of molecular weight and molecular weight distribution with conversion (b), and GPC traces with conversion (c) for AGET ATRP of OEOMA300 in water at 30 °C with $CuCl_2$/TPMA complex. Conditions: $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuCl_2/TPMA]_0/[AscA]_0 = 300/1/1/0.15$ (entry 6). The straight line is theoretically calculated molecular weight.

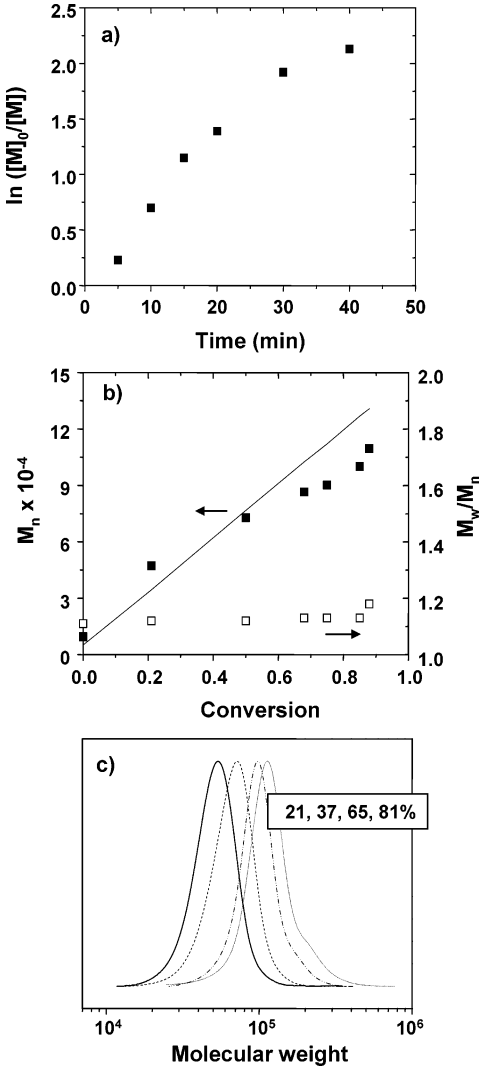


Figure 7. First-order kinetic plot (a), evolution of molecular weight and molecular weight distribution (b), and GPC traces with conversion (c) for AGET ATRP of OEOMA475 in water at 30 °C. Conditions: $[OEOMA475]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0/[AscA]_0 = 300/1/0.5/0.075$; water/OEOMA475 = 2.5/1 v/v, $[AscA]_0 = 0.15$ mM and $[Cu(II)]_0 = 1.01$ mM (entry 9).

Table 2. Conversion and Molecular Weight Data of P(OEOMA300) Prepared by AGET ATRP in Water at 30 °C with $CuBr_2$/Bpy Complex[a]

time [min]	conv	$M_{n,theo}$[b]	$M_{n,GPC}$	M_w/M_n
10	0.58	55 300	79 400	1.34
17	0.71	67 600	94 800	1.53

[a] $[OEOMA300]_0/[PEO5000\text{-}Br]_0/[CuBr_2]_0/[bpy]_0/[AscA]_0 = 300/1/0.5/1/0.075$. [b] $M_{n,theo}$ = MW (PEO5000-Br) + MW(OEOMA300) × ($[OEOMA300]_0/[PEO5000\text{-}Br]_0$) × conversion.

reached a plateau at around 50%. This limited conversion can be caused by the use of either too low concentrations of Cu(II) complex or ascorbic acid. The results reported in the previous sections suggested that further increase of the relative ratio of ascorbic acid to Cu(II) complex reduces control with the occurrence of bimodal distribution. Alternatively, the lower dilution by water would retain the same ratio of ascorbic acid to Cu(II) complex but would increase their concentrations. For AGET ATRP of OEOMA475 (entry 9, Table 3), the ratio of water/OEOMA475 was decreased from 3.8/1 (v/v) to 2.5/1 (v/v). Conversion increased up to 85% (Figure 7a). The polymerization medium became too viscous to stir after 20 min. Molecular weight increased with conversion. The values obtained by GPC with PMMA standards were close to the theoretical values; however, they appeared to be smaller than the theoretical values above 60% conversion. However, molecular weight distribution was narrow, $M_w/M_n = 1.12-1.20$ (Figure 7b). The GPC traces of P(OEOMA475) were monomodal, with a very slight shoulder when conversion was above 80% (Figure 7c).

Table 3. Concentrations of Ascorbic Acid and Cu(II) Complex and Properties of Final P(OEOMA475) Prepared by AGET ATRP Targeting DP = 300 in Water at 30 °C[a]

entry	water/OEOMA475 (v/v)	$CuBr_2$ [mM][b]	AscA [mM][b]	time [min]	conv	$M_{n,theo}$[c]	$M_{n,GPC}$	M_w/M_n
8	3.8/1	0.74	0.11	40	0.46	70 800	67 300	1.13
9	2.5/1	1.01	0.15	40	0.85	126 700	96 000	1.18

[a] $[OEOMA475]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0 = 300/1/0.5$ with 15 mol % ascorbic acid of Cu(II) complex. [b] Concentration in water + OEOMA475. [c] $M_{n,theo}$ = MW (PEO5000-Br) + MW(OEOMA475) × ($[OEOMA475]_0/[PEO5000\text{-}Br]_0$) × conversion.

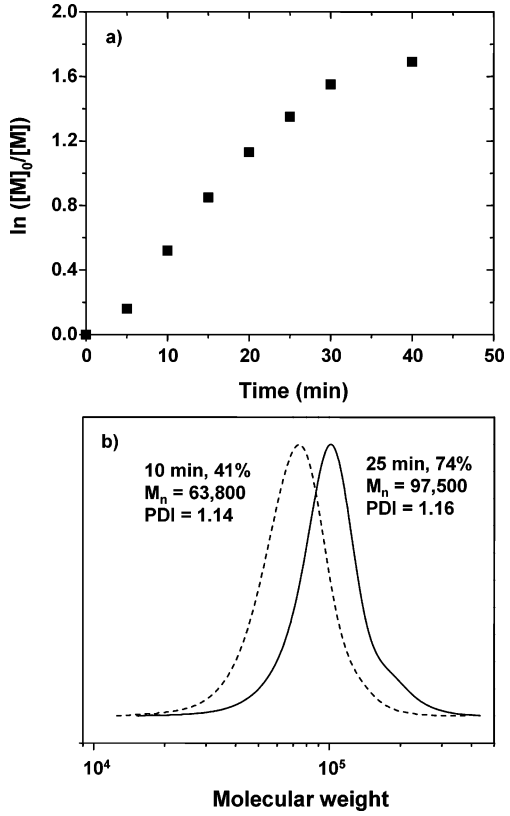


Figure 8. First-order kinetic plot (a) and evolution of GPC traces (b) of random copolymers consisting of OEOMA300 and OEOMA475 with conversion for AGET ATRP in water at 30 °C. Conditions: $[OEOMA300]_0/[OEOMA475]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0/[AscA]_0$ = 184/116/1/0.5/0.075; water/OEOMA = 3.8/1 v/v; $[AscA]_0$ = 0.14 mM and $[Cu(II)]_0$ = 0.94 mM.

Synthesis of Random Copolymers. The random copolymers of OEOMA300 and OEOMA475 with targeted DP = 300 were prepared by AGET ATRP in water at 30 °C with the following molar ratio: $[OEOMA300]_0/[OEOMA475]_0/[PEO5000\text{-}Br]_0/[CuBr_2/TPMA]_0/[AscA]_0$ = 184/116/1/0.5/0.075. Similar to homopolymerization of OEOMA300 (entry 3, Figure 4), first-order kinetic plot shows that conversion increased with time and reached up to 80% in 40 min (Figure 8a). The evolution of GPC traces indicates a gradual increase of molecular weight of polymers with conversion (Figure 8b). In addition, monomodal, narrow molecular weight distribution was obtained (M_w/M_n <1.2). The normalized peaks from the unreacted residual macromonomers overlapped to some extent in the GPC chromatograms appeared to remain constant, as shown in the Supporting Information. This indicates the formation of random copolymers of OEMA300 and OEOMA475.

Conclusions

AGET ATRP was successfully applied to the aqueous ATRP of water-soluble OEOMA macromonomers targeting a DP = 300 at ambient temperature (30 °C). AGET ATRP led to the synthesis of well-controlled homopolymers and random copolymers of OEOMA with relatively high molecular weight and narrow molecular weight distribution at high conversion. The concentration of both Cu(II) complex and ascorbic acid added to reaction mixture was varied to achieve control over aqueous AGET ATRP of OEOMA300. The use of either too large amounts of Cu(II) complex or ascorbic acid resulted in polymers with bimodal molecular weight distribution. Too small amounts of Cu(II) complex or ascorbic acid resulted in limited conversion. The ATRP rate was slower but better controlled with the $CuCl_2$/TPMA complex than with the $CuBr_2$/TPMA complex. P(OEOMA300) prepared in the presence of $CuBr_2$/bpy had a broader molecular weight distribution than when prepared with $CuBr_2$/TPMA complex. The relative amount of water to OEOMA475 was varied to synthesize well-controlled P(OEOMA475) at high conversion. In addition, well-defined random copolymers were prepared by AGET ATRP of a 1:1 wt/wt mixture of OEOMA300 and OEOMA475.

The above results proved that homogeneous aqueous ATRP can be controlled. The relative and absolute concentrations of the Cu(II)/ligand complex and ascorbic acid are important for control over AGET ATRP in water. In this context, the results provide a starting point for aqueous ATRP to prepare well-controlled, high molecular weight, water-soluble polymers. They also provide a guideline for incorporation of P(OEOMA) segments into materials targeting high value applications, such as molecular brushes and smart materials,[31] soft elastomers,[19] and cyclodextrin-based hydrogels.[32]

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Supporting Information Available: GPC traces of residual unreacted macromonomers (OEOMA300 and OEOMA495) in samples taken at different time intervals. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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