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Dedicated to the 80th Birthday of Dr. Otto Vogl, Herman F. Mark Professor Emeritus

Methylaluminoxane as a Reducing Agent for Activators Generated by Electron Transfer ATRP

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Activators generated by electron transfer (AGET) atom transfer radical polymerization (ATRP) of *n*-butyl acrylate (*n*BA) was carried out in the presence of methylaluminoxane (MAO) as a new reducing agent for Cu(II) complexes. The molecular weights of the produced poly(*n*BA) increased with *n*BA conversions with low polydispersities (~ 1.2) and they were close to the theoretical values. The polymerization proceeded successfully using five-fold excess of MAO over Cu(II) complex. UV-VIS measurements confirmed that MAO reduced the Cu(II) complex. When the mixture of MAO was monitored by UV-VIS spectroscopy, a decrease of the peak absorbing at 950 nm attributed to CuCl₂/tri(2-pyridylmethyl)amine (TPMA) complex in *N,N*-dimethylformamide (DMF) at room temperature was observed as soon as MAO was added.

Keywords: ATRP; reducing agents; MAO; AGET

1 Introduction

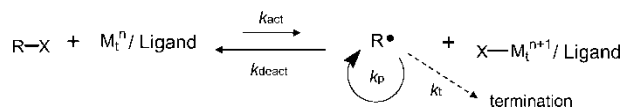
Controlled/living polymerization systems are the robust methods to prepare well-defined polymers. Among them, atom transfer radical polymerization (ATRP) is one of the powerful techniques to synthesize polymers with controlled molecular weights and low polydispersities. Since the Cu-mediated ATRP technique was discovered in 1995 (1), ATRP has been applied to a wide range of monomers (2–5) and the synthesis of various polymers such as gradient (6), alternating (7), block (8), graft (9) and star (10) polymers. A general mechanism of ATRP is shown in Scheme 1.

The radicals are generated through a reversible redox process catalyzed by a transition metal complex (M_t^n /Ligand) that undergoes one electron oxidation with abstraction of a radically transferable atom or group, X, from a dormant species, R-X. Then, the growing radicals react reversibly with the oxidized metal complex ($X-M_t^{n+1}$ /Ligand) to reform the dormant species and the metal complex (M_t^n /Ligand), and the polymerization proceeds. This process occurs with a rate constant of activation, k_{act} , and

deactivation, k_{deact} , and polymer chains grow with a rate constant of k_p . Termination reactions, k_t , also occur due to radical coupling and disproportionation. Well-defined polymers using the ATRP technique can be obtained if k_{deact} is large enough to reduce the probability of the termination reactions and initiation is fast in comparison with propagation. Although ATRP can provide many well-defined polymers, there are also some problems. One of the problems is that since ATRP proceeds with strongly reducing catalysts, the metal complex in a lower oxidation state can be easily oxidized by air to the corresponding higher oxidation state. To overcome this problem, reducing agents such as tin(II) 2-ethylhexanoate (Sn(EH)₂) (11–13), ascorbic acid (14), phenol (15), thiophenol (16) and triethylamine (17) were used to conduct ATRP with higher oxidation state metal complexes (Cu(II) complexes). This method, which has been termed “activators generated by electron transfer” for ATRP (AGET ATRP), is a very useful technique because oxidatively stable metal complexes (higher oxidation state metal complexes), which are easier to handle than lower oxidation metal complexes can be used.

MAO [$[-Al(Me)-O-]_n$, $n = 5\sim 20$], which is an oligomeric compound prepared by controlled hydrolysis of AlMe₃, has been known as a highly efficient cocatalyst for coordination polymerization of ethylene, propylene and higher α -olefins when combined with group 4 metallocene catalysts (18).

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Sch. 1. Mechanism of ATRP.

The proposed mechanism of activating MX_2L (M; metal, X; halogen, L; ligand) with MAO is shown in Scheme 2. MX_2L is monoalkylated by MAO to give $\text{M}(\text{Me})\text{XL}$ and the halogen of the resulting $\text{M}(\text{Me})\text{XL}$ is abstracted by MAO to form a catalytically active cationic species, indicating that a catalyst complex MX_2L is reduced to $\text{M}(\text{Me})\text{L}$ by MAO (19). Taking into account this mechanism, MAO has a possibility to be used as a reducing agent for AGET ATRP. It was previously reported that a $\text{Cu}(\text{II})\text{Cl}_2/1,2\text{-bis-(4,4-dimethyl-2-oxazolin-2-yl)ethane}$ complex was reduced to a $\text{Cu}(\text{I})$ by MAO according to an EPR study (20). These results encouraged us to use MAO as a reducing agent for complexes active in ATRP and apply it for AGET ATRP. Both model reactions and AGET ATRP of *n*-butyl acrylate (*n*BA) using MAO as reducing agent will be reported in this paper.

2 Experimental

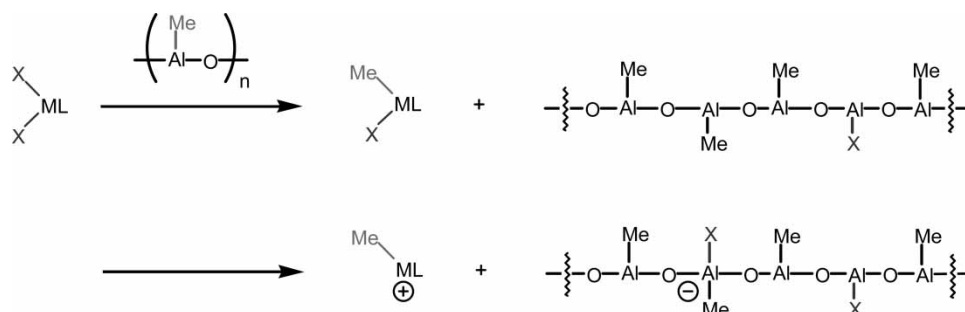
2.1 Materials

n-Butyl acrylate (*n*BA) (Acros, 99%) was passed through a column filled with basic alumina, dried over calcium hydride, and distilled under reduced pressure. Anisole (Aldrich, 99%) was dried over calcium hydride, and distilled under reduced pressure. Tri(2-

pyridylmethyl)amine (TPMA) was synthesized following the previously reported procedure (21, 22). Ethyl 2-bromoisobutyrate (EtBrIB) (Acros, 98%), copper(II) chloride (Acros, 99%), methylaluminoxane (MAO) (Aldrich, 10 wt% in toluene), *N,N*-dimethylformamide (DMF) (Aldrich, 99%) were used as received.

2.2 Analysis

Molecular weight and polydispersity were determined by (GPC), conducted with a Waters 515 pump and Waters 2414 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 polystyrene standards were used for calibration. Conversion of *n*BA was determined using a Shimadzu GC 14-A gas chromatograph equipped with a FID detector using a J&W Scientific 30 m DB WAX Megabore column with anisole as an internal standard. Injector and detector temperatures were kept constant at 250°C . Analysis was carried out isothermally at 60°C for 2 min followed by an increase of temperature to 180°C at a heating rate of $40^\circ\text{C}/\text{min}$ and holding at 180°C for 5 min. Conversion was calculated by detecting the decrease of the monomer peak area relative to the peak areas of the standards. GC-MS analysis was performed on a Hewlett-Packard Agilent 6890-5973 GC-MS workstation. The GC column was a Hewlett-Packard fused silica capillary column cross-linked with 5% phenylmethylsiloxane. Analysis was carried out isothermally at 40°C for 5 min followed by an increase of temperature to 200°C at a heating rate of $20^\circ\text{C}/\text{min}$ and holding at 200°C for 2 min.



Sch. 2. Mechanism of activation of MX_2L with MAO.

Table 1. Experimental conditions and properties of *n*BA by AGET ATRP using MAO^a

Entry	Molar ratios					Time (min)	Conv. (%)	M_n theo. ^b	M_n GPC	M_w/M_n
	<i>n</i> BA	EtBrIB	CuCl_2	TPMA	Al/Cu					
1	200	1	0.1	0.1	10	120	72	18300	16600	1.14
2	200	1	0.1	0.1	5	135	74	19000	15700	1.14

^a $T = 60^\circ\text{C}$ in anisole (*n*BA/anisole = 1/0.02 v/v).

^b M_n theo. = $[\textit{nBA}]_0/[\text{EtBrIB}]_0 \times \text{conversion} \times \text{molecular weight of } \textit{nBA}$.

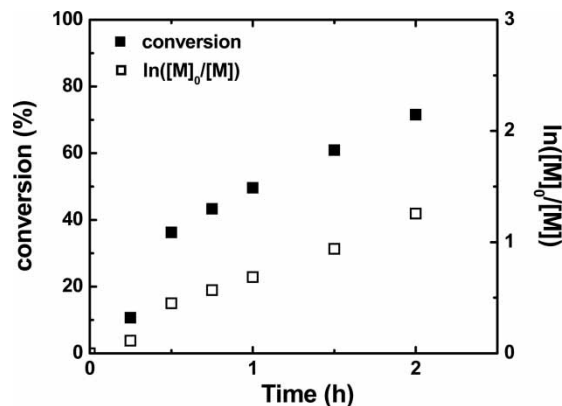


Fig. 1. Kinetic plots for AGET ATRP of *n*BA using MAO. Experimental conditions: *n*BA/EtBrIB/CuCl₂/TPMA/ = 200/1/0.1/0.1, Al/Cu = 10, *T* = 60°C in anisole (*n*BA/anisole = 1/0.02 v/v) (Table 1, Entry 1).

2.3 General Procedure for the UV-VIS Measurements

CuCl₂ (3.36 mg, 0.025 mmol) and TPMA (7.26 mg, 0.025 mmol) were added to a Schlenk flask joined to a quartz UV cuvette, and then the Schlenk flask was sealed. The flask was evacuated and back-filled with nitrogen three times. MAO (166 μL, 0.25 mmol) solution was added to 5 mL of degassed DMF and the solution was added to the flask via a degassed syringe through the side arm. The absorbance at a wavelength corresponding to CuCl₂ was monitored at timed intervals. The spectroscopic measurements were performed on a Lambda 900 (Perkin-Elmer) UV/vis/NIR spectrometer. The other sample (DMF solution of CuCl₂ and TPMA) was prepared and studied in a similar fashion.

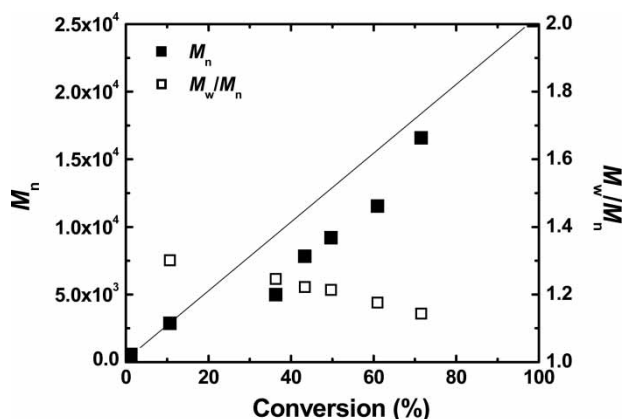


Fig. 2. Molecular weights and polydispersities of poly(*n*BA) with the change of conversions of AGET ATRP using MAO. Experimental conditions: *n*BA/EtBrIB/CuCl₂/TPMA/ = 200/1/0.1/0.1, Al/Cu = 10, *T* = 60°C in anisole (*n*BA/anisole = 1/0.02 v/v) (Table 1, Entry 1).

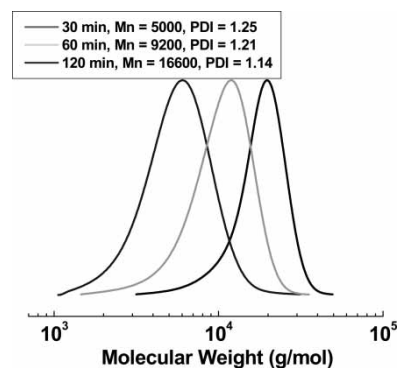


Fig. 3. Evolution of molecular weight distribution of AGET ATRP using MAO. Experimental conditions: *n*BA/EtBrIB/CuCl₂/TPMA/ = 200/1/0.1/0.1, Al/Cu = 10, *T* = 60°C in anisole (*n*BA/anisole = 1/0.02 v/v) (Table 1, Entry 1).

2.4 General Procedure for AGET ATRP of *n*BA

The ligand TPMA (10.0 mg, 0.0350 mmol) and CuCl₂ (2.35 mg, 0.0175 mmol) were added to a Schlenk flask. To this mixture, *n*BA (5.00 mL, 34.9 mmol) and anisole (0.100 mL) were transferred via degassed syringe. The flask was tightly closed and the mixture was degassed by three freeze-pump-thaw cycles. The resulting mixture was stirred for 10 min and MAO solution (116 μL, 0.175 mmol) was added. Then, EtBrIB (26.2 μL, 0.175 mmol) initiator was added to initiate the polymerization. An initial sample was taken and the sealed flask was placed in thermostated oil bath at 60°C. Samples were taken at timed intervals and analyzed by gas chromatography (GC) and gel permeation chromatography (GPC) to follow the progress of the reaction.

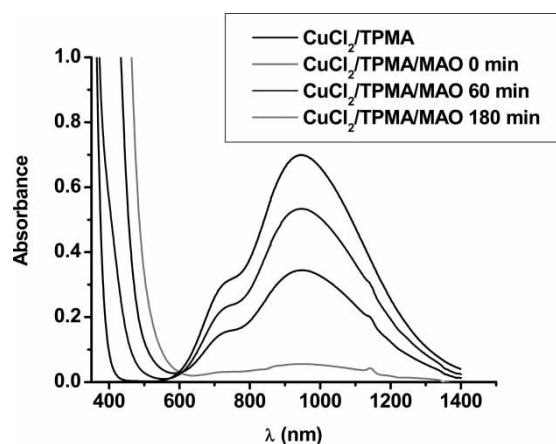
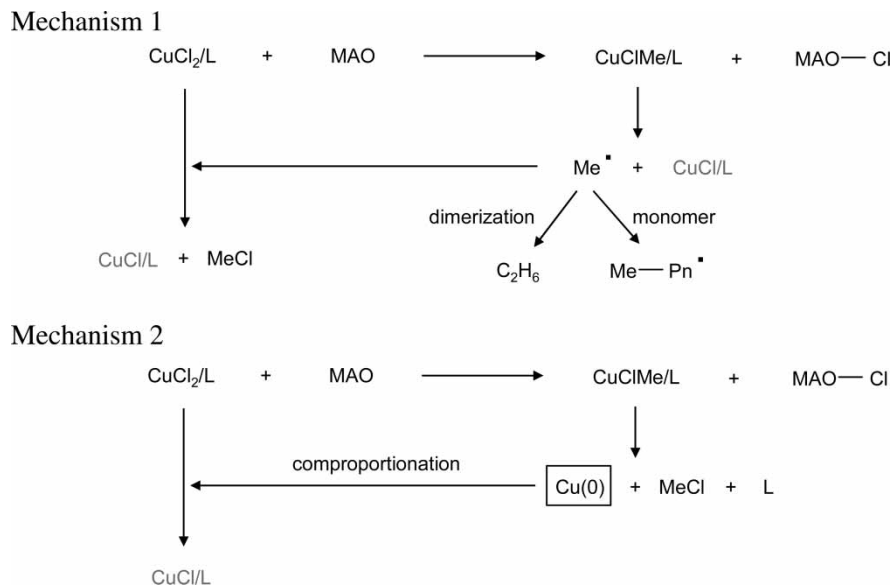


Fig. 4. UV-VIS spectra of the DMF solution of CuCl₂, TPMA and MAO at room temperature; [CuCl₂] = 5.0 mM; CuCl₂/TPMA = 1.0/1.0, Al/Cu = 10.



Sch. 3. Plausible Reduction Mechanisms of $\text{Cu(II)Cl}_2/\text{L}$ with MAO.

3 Results and Discussion

AGET ATRP is a promising method because it employs oxidatively stable transition metal complexes (23–28). Reducing agents react quickly with the transition metal complex and efficiently generate *in situ* the ATRP activators. Although MAO has been demonstrated to reduce some Cu(II) complexes (20), it has not been certain whether MAO could be used to ATRP relevant complexes and applied efficiently in AGET ATRP. To investigate MAO as a new reducing agent, AGET ATRP of *n*BA was conducted. The conditions and results are shown in Table 1. AGET ATRP of *n*BA was conducted using CuCl_2 , TPMA as a ligand, MAO and EtBrIB. The polymerization proceeded successfully in the presence of 10 times larger amount of MAO compared to CuCl_2 (Table 1, Entry 1). *n*BA was consumed constantly and the monomer conversion reached 72% in 2 h with a low M_w/M_n value (1.14) (Figure 1). The molecular weights of the produced poly(*n*BA) increased linearly with *n*BA conversions, and they remained close to the theoretical values (Figure 2). The GPC curves of the poly(*n*BA) were monomodal and shifted symmetrically with the increase of molecular weight (Figure 3). These results suggest that the ATRP activator was generated efficiently *in situ* by MAO to obtain the well-controlled polymer. Reducing the amount of MAO from the ratio of $\text{Al}/\text{Cu} = 10$ to 5 did not significantly affect the polymerization results (Table 1, Entry 2). In olefin polymerization, typically a few hundreds or thousands fold excess of MAO over metal complexes is needed to form catalytically active species in olefin polymerization (19). In AGET ATRP of *n*BA, a five-fold excess of MAO over CuCl_2 was enough to form the sufficient amount of the activator to start ATRP.

UV-VIS measurements were performed to follow the absorption spectrum of $\text{CuCl}_2/\text{TPMA}$ in the presence of

MAO (Figure 4). The absorption at 950 nm, attributed to $\text{CuCl}_2/\text{TPMA}$ in DMF at room temperature, started to decrease immediately when MAO was added and gradually decreased as the reaction proceeded. The consumption of the Cu(II) complex indicated that MAO reduced it to Cu(I) state. The reduction could proceed in a way similar to that presented in the first step in Scheme 2, generating $\text{Cu(II)ClMe}/\text{TPMA}$ species. This metastable complex could decompose to form the activator $\text{Cu(I)Cl}/\text{TPMA}$ and methyl radicals (could abstract chlorine from other $\text{Cu(II)Cl}_2/\text{TPMA}$, dimerize to form ethane, or initiate polymerization). Alternatively, $\text{Cu(II)ClMe}/\text{TPMA}$ could decompose to form MeCl and Cu(0) , that could subsequently comproportionate with $\text{Cu(II)Cl}_2/\text{TPMA}$ to form $\text{Cu(I)Cl}/\text{TPMA}$. Indeed, when the mixture of $\text{Cu(II)Cl}_2/\text{TPMA}$ and MAO in DMF was analyzed by GC-MS, a compound with $m/z = 50, 52$, corresponding to MeCl was detected. Thus, a plausible reduction of Cu(II) species is presented in Scheme 3, followed by the AGET ATRP process with MAO as a reducing agent.

4 Conclusions

MAO was successfully applied as a reducing agent in AGET ATRP. Polymerization of *n*BA was well-controlled providing polymers with predetermined molecular weights and with low M_w/M_n values. In UV-VIS measurements, the absorption of $\text{CuCl}_2/\text{TPMA}$ in DMF at room temperature started to decrease immediately after MAO was added and gradually decreased as the reaction proceeded, suggesting that MAO reduced the CuCl_2 complex and generated Cu(I) activators. AGET ATRP is a very promising technique because it can be conducted with oxidatively stable metal complexes.

Additionally, since MAO has been used in industry as a cocatalyst in olefin polymerization, it could be easily applied for commercial AGET ATRP processes.

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