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# $CuBr_2$/$Me_6$TREN-mediated living radical polymerization of methyl methacrylate at ambient temperature

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## ABSTRACT

A universal nitrogen based ligand, tris[2-(dimethylamino) ethyl] amine ($Me_6$TREN), was firstly employed as both reducing agent and ligand for atom transfer radical polymerization with activators regenerated by electron transfer (ARGET ATRP) of methyl methacrylate (MMA) in bulk and solution, using $CuBr_2$ as the catalyst and 2-bromoisobutyrate as the initiator. Remarkably high activity catalytic system ($CuBr_2$/$Me_6$TREN) enabled the ambient temperature polymerization and thus biradical termination reactions were low. The polymerization exhibited typical living radical polymerization features, including pseudo first-order kinetics of polymerization, linear increase in the molecular weight versus monomer conversion, and low polydispersity index values. Moreover, effects of solvent and reaction temperature on the polymerization were investigated in detail. The rate of polymerization increased with reaction temperature and the apparent activation energy of the polymerization was calculated to be 51.11 kJ/mol. Gel permeation chromatography and $^1$H NMR analyses as well as chain extension experiment confirmed the living chain-end functionality.

## 1. Introduction

Poly(methyl methacrylate) (PMMA), as a commercially important polymeric material, has been widely applied in a variety of fields for years, ranging from plastics industry, bio-medicine, and semiconductor research to optical media and γ-ray resistance. Generally, radical polymerization is used to synthesize such methyl methacrylate (MMA) polymers [1–6]. However, due to the lack of controlled/living polymerization features, this methodology can not produce well-defined PMMA with predictable molecular weight (MW) and low polydispersity index (PDI). The advent of living radical polymerization (LRP) techniques, e.g., atom transfer radical polymerization (ATRP) [7–18], enables the preparation of well-defined PMMA. Unfortunately, the original ATRP technique usually requires the use of a very high concentration of low valence metal catalyst which is subject to oxidation.

More recently, a novel ATRP process termed "activator regenerated by electron transfer" (ARGET) ATRP has attracted a great deal of attention because of its lower catalyst loading (ppm levels with respect to the monomer) and better tolerance toward oxygen [19–22]. Based on the mechanism of ARGET ATRP, an excess amount of reducing agent relative to metal catalyst is utilized to convert higher oxidation state deactivators to lower oxidation state activators (Scheme 1). In total, reducing agent plays a crucial role in ARGET ATRP. To date, a wide range of reducing agents have been successfully exploited, such as tin(II) 2-ethylhexanoate [21], glucose [21,22], ascorbic acid [23], phenylhydrazine [24], phenol [25], alcohols [26], nitrogen-containing ligands [27], monomers [28], and zero-valent metals [29,30]. Meanwhile, the used ligand significantly influences the ARGET ATRP process. First, it is responsible for solubilizing the transition metal salt in the organic media. Second, the appropriate ligand can efficiently adjust the redox potential of the metal center for suitable reactivity and dynamics for the atom transfer [31]. The typical ligands used for ARGET ATRP of MMA include [tris(2-dimethylamino)ethylamine] ($Me_6$TREN), tris[(2-pyridyl)methyl]amine, and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA). As described above, reducing agent and ligand are the two indispensable components for this new ATRP system. Therefore, the issue of whether a compound can serve as both the reducing agent and the ligand has been attracting great interest.

Initially, Shen and his coworkers reported that tertiary amines, triethylamine and tributylamine, could efficiently reduce Cu(II) to Cu(I) species in the AGET ATRP of MMA [32,33]. The nitrogen-based ligands, such as *N*,*N*,*N*′,*N*′-tetramethylethylenediamine,

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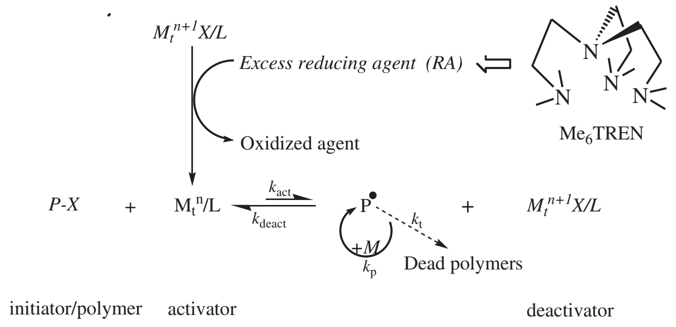

**Scheme 1.** Proposed mechanism for ARGET ATRP (the starting components are shown as the italic text).

*N*,*N*,*N′*,*N″*,*N‴*,*N‴′*-hexamethyltriethylenetetramine, and PMDETA, also possess tertiary amine groups. Subsequently, Matyjaszewski's and Lai's groups detailedly investigated the A(R)GET ATRP of MMA using an excess of those nitrogen based ligands in the absence of any additional reducing agents [27,34]. In all cases, the MMA polymerizations exhibited typical features of LRP and yielded the controlled polymers. However, to the best of our knowledge, a highly active ligand with four tertiary amine groups, $Me_6TREN$, has never been explored for the ARGET ATRP of MMA. The only reference is the efficient reduction of $Cu(II)Cl_2$ to Cu(I)Cl with 10-fold excess $Me_6TREN$ as the reducing agent in the ARGET ATRP of *n*-butyl acrylate (BA) at 60 °C, reported by Matyjaszewski and his coworkers [24]. Although BA polymerization was well controlled in terms of molecular weight, control over molecular weight distribution was very poor (PDI = 1.83 for a monomer conversion of 86%). Furthermore, it must be kept in mind that $Me_6TREN$ was universally added to metal at several times molar excess in a typical ARGET ATRP system [35].

The present paper report the facile ARGET ATRP of MMA with $Me_6TREN$ as both the reducing agent and the ligand at ambient temperature. The polymerization was well controlled with respect to molecular weight and PDI under the optimized conditions. The living radical polymerization characteristics have been confirmed by a combination of polymerization kinetic studies and chain end-group analyses of the resulting polymer.

## 2. Experimental

### 2.1. Materials

MMA was washed with 5% NaOH solution followed by deionized water, distilled under reduced pressure, and stored at −20 °C prior to use. Acetonitrile (MeCN), tetrahydrofuran (THF), and dichloromethane ($CH_2Cl_2$) were dried over anhydrous calcium chloride and freshly distilled. Dimethyl sulfoxide (DMSO) and N, N-dimethylformamide (DMF) were distilled under reduced pressure before use. Ethylene carbonate (EC, Aladdin), anhydrous cupric bromide ($CuBr_2$, Alfa Aesar), and ethyl 2-bromoisobutyrate (EBiB, Aladdin) were used as received. Tris [2-(dimethylamino) ethyl] amine ($Me_6TREN$) was synthesized according to a literature method [36,37].

### 2.2. Polymerization

A typical polymerization procedure is as follows: a dry Schlenk tube was charged with MMA (2 mL), DMSO (1 mL), $Me_6TREN$ (21.7 mg, 0.0942 mmol), $CuBr_2$ (2.10 mg, 0.00942 mmol), and EBiB (18.4 mg, 0.0152 mmol). The tube was sealed with a rubber septum, and degassed by three freeze–pump–thaw cycles to remove the oxygen, and then immersed in a thermostated oil bath at designed temperature. After various time intervals, the isolated solution was diluted with THF. Subsequently, the reaction mixture was cooled to ambient temperature using ice-water mixture and then precipitated using large amounts of methanol/HCl (v/v, 100/0.1). The obtained PMMA was filtrated, washed with methanol and dried under vacuum at 50 °C until a constant weight.

### 2.3. Chain extension of PMMA

The following chain-extended recipe was used: a predetermined quantity of obtained PMMA (319.7 mg, 0.0471 mmol) and MMA (1 mL) were dissolved in DMSO (1 mL). The mixture was stirred magnetically for 30 min to prepare a homogenous solution in Schlenk tube, and then $Me_6TREN$ (10.9 mg, 0.0471 mmol) and $CuBr_2$ (1.05 mg, 0.00471 mmol) were rapidly added. The tube was tightly sealed with a rubber septum. The rest of the procedure was similar to the above.

### 2.4. Characterization

The monomer conversions were calculated gravimetrically.$^1$H NMR spectra of PMMA were obtained on a Bruker 300 MHz Spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference at ambient temperature. Samples were diluted before measuring with THF. The number-average molecular weights ($M_{n,GPC}$) and PDI values of the obtained PMMA samples were measured by gel permeation chromatography (GPC) system equipped with a Waters 510 HPLC pump, three Waters Ultrastyragel columns (500, $10^3$, and $10^5$), and a Waters 2414 RI detector. THF was used as the eluant and the flow rate was 1.00 ml/min. PMMA standards were used for calibration. Theoretical molecular weights ($M_{n,th}$) of the resulting PMMA was calculated by the following equation:

$$M_{n,th} = \frac{[MMA]_0 \times Conv. \times M_{MMA}}{[EBiB]_0} + M_{EBiB}$$

where $[MMA]_0$ and $[EBiB]_0$ are the initial concentrations of MMA and EBiB, respectively. $M_{MMA}$ and $M_{EBiB}$ correspond to the molecular weights of MMA and EBiB. *Conv.* is the monomer conversion.

## 3. Results and discussion

### 3.1. Copper-mediated living radical polymerization of MMA with $Me_6TREN$ as the reducing agent at ambient temperature

In general, the most important characteristics of a living radical polymerization embrace pseudo first-order kinetics of polymerization, controlled molecular weight, low PDI, linear evolution of molecular weight with monomer conversion, and perfect or near perfect chain-end fidelity [38]. The polymerizations of MMA using $Me_6TREN$ as the reducing agent with a molar ratio of $[MMA]_0/[EBiB]_0/[Me_6TREN]_0/[CuBr_2]_0 = 200/1/1/0.1$ were first conducted in bulk at 25 °C, and the results are presented in Table 1 (entries 1–4) and Figs. 1 and 2. Obviously, bulk polymerization exhibits a completely different kinetic behavior consisting of two linear domains with two different apparent rate constant of propagation ($k_p^{app}$) values, the first with $k_p^{app} = 6.74 \times 10^{-6}$ s$^{-1}$, and the second with $k_p^{app} = 3.15 \times 10^{-5}$ s$^{-1}$ (Fig. 1). The result may be attributed to two factors. On one hand, the solubility of the complexe $Cu(II)Br_2/Me_6TREN$ in the MMA medium was very poor [39], as can be seen from the fact that most of them kept precipitated throughout the polymerization. The Cu(II) species in the heterogenous mixture did not efficiently deactivate the active radicals, thus deteriorating the