

# Functional initiators for both ATRP and ROP catalyzed by iron(III) catalyst

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**Abstract.**  $\alpha$ -Trichloromethyl benzyl alcohol was successfully used as initiators for both AGET ATRP and ROP reactions, which was catalyzed by only one non-toxic and very cheap catalyst iron(III) chloride. The corresponding polymers PMMA and PCL were characterized by <sup>1</sup>H NMR, and their molecular mass were calculated as 7.53 kDa and 10.08 kDa, respectively.

## 1. Introduction

Living polymerization methods have been extensively developed and applied in many areas such as polymer preparation, materials designing, life science, drug manufacturing and delivery, etc [1-3]. For different living polymerization approaches, living radical polymerizations, such as ATRP, reversible addition-fragmentation chain transfer polymerization (RAFT), and nitroxide mediated radical polymerization (NMP), are the mostly studied and used to prepare functional macromolecules [4-6]. Ring opening polymerization (ROP) is another powerful tool to produce many kinds of polymers, e.g., polycaprolactone (PLC), polyethylene oxide (PEO), etc [7-10].

To incorporate polymer segments which are incompatible into one macromolecule, strategies for combination of living polymerization and ROP are utilized, thus various functional polymers which are previously inaccessible are synthesized [11-12]. However, these reaction systems are always complex due to the presence of different components. To simplify the reaction system, multi-functional molecules are designed and used in literature [13].

In this study, a synthesized molecule is used as an initiator for both AGET ATRP and ROP reactions, which make it possible to prepare block copolymers simultaneously or in one pot. Furthermore, both activator-generated by electron transfer atom transfer radical polymerization (AGET ATRP) and ROP reactions can be catalyzed by only one catalyst.

## 2. Experimental

### 2.1. Instruments and reagents

Nuclear magnetic resonance (NMR) was measured by a BrukerAV 400MHz nuclear magnetic resonance meter (CDCl<sub>3</sub> as solvent, TMS as internal standard).

Chloroform, benzaldehyde, tetrabutylammonium bromide (TBAB), Iron(III) chloride hexahydrate,  $\epsilon$ -caprolactone ( $\epsilon$ -CL), dichloromethane, petroleum ether (PE), ethyl acetate (EA), *N,N,N',N'*-tetramethyl ethylene diamine (TMEDA), ascorbic acid (AA), *N,N*-dimethyl formamide



(DMF) and dimethyl sulfoxide (DMSO) are all AR grade and used as received. Methyl methacrylate (MMA) was treated with basic ion-exchangeable resin to remove inhibitor before use.

### 2.2. Synthesis of $\alpha$ -trichloromethyl benzyl alcohol (**1**)

Synthesis of this initiator was easily finished according to our previous work [14], i.e., the mixture of benzaldehyde and chloroform under strong basic conditions furnished compound **1** in moderate yield.

### 2.3. Preparation of poly(methyl methacrylate) (PMMA) (**2**) using **1** as an initiator and $\text{FeCl}_3$ as a catalyst

The material MMA (10.0 g, 100 mmol), iron(III) chloride hexahydrate (0.54 g, 2 mmol), the initiator  $\alpha$ -trichloromethyl benzyl alcohol (**1**) (0.23 g, 1 mmol), ascorbic acid (0.18 g, 1 mmol), and TMEDA (0.17 g, 1 mmol) were added to the solvent DMSO (80 mL). The resulting mixture was stirred at 80 °C for 12 h under the protection of  $\text{N}_2$  atmosphere. After the reaction was completed, excess cold methanol was poured, and the resulting precipitate was filtered to afford crude polymer. The crude product was purified on neutral  $\text{Al}_2\text{O}_3$  column to provide a white like solid (7.33 g), conversion 71%.

### 2.4. Preparation of poly( $\epsilon$ -caprolactone) (PCL) (**3**) using **1** as an initiator and $\text{FeCl}_3$ as a catalyst

Into a 250 mL of three-necked flask were added  $\alpha$ -trichloromethyl benzyl alcohol (**1**) (0.23 g, 1 mmol), the monomer  $\epsilon$ -caprolactone (1.14 g, 10 mmol), iron(III) chloride hexahydrate (0.54 g, 2 mmol) and the solvent DMSO (30 mL). The mixture was stirred at ambient temperature for 10 h under nitrogen protection. Then, the mixture was poured into cold methanol to form brown-red solid, after filtration and drying, the solid product (0.94 g) was obtained with conversion of 62%.

## 3. Results and discussion

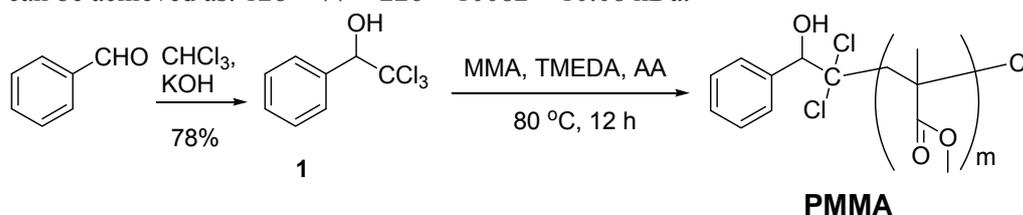
### 3.1. Preparation of PMMA under AGET ATRP conditions catalyzed by $\text{FeCl}_3$

The compound  $\alpha$ -trichloromethyl benzyl alcohol (**1**) proved to be a good initiator under SET-LRP conditions, and preparation of the corresponding polymer was discussed in our previous work [14]. However, in conventional ATRP or SET-LRP, copper catalysts (e.g.,  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuCl}_2$ ,  $\text{CuBr}_2$ ,  $\text{Cu}(0)$ ) are always involved. It is known that copper is toxic and excess copper content in bodies will lead to diseases such as copperiedus. Thus, copper-catalyzed polymerizations are limited especially in preparation of special polymers such as biomedical materials. Therefore, strategies for replacing copper catalysts in atom transfer radical polymerization (ATRP) or related polymerization reactions are developed in the past decade [15]. For example, Zhu's research group reported many work on iron-mediated living radical polymerizations in recent years. Their latest work is use of ppm level organometallic catalyst iron(III) acetylacetonate in toluene to prepare PMMA in homogenous phase [16]. Herein, we investigated polymerization of methyl methacrylate using iron(III) chloride as the catalyst and  $N,N,N',N'$ -tetramethyl ethylene diamine (TMEDA) as the ligand. When the reaction mixture was stirred at 80 °C for 12 h, the corresponding polymer PMMA was readily obtained in moderate conversion (Scheme 1). After purification on alumina column, the PMMA sample was characterized by  $^1\text{H}$  NMR, and the spectrum was shown in Figure 1b. As comparison, Figure 1a indicated  $^1\text{H}$  NMR spectrum of the initiator  $\alpha$ -trichloromethyl benzyl alcohol (**1**). The number of proton on aryl ring is five, so the value of integration of peaks at 7.3-7.7 ppm is designated as five. Thus, integration value of the single peak at 3.60 ppm is 219, which is the signal of protons of methoxy groups in PMMA unit. Therefore, the number of MMA unit can be calculated as  $219/3 = 73$ . The molecular mass of PMMA is  $73 \times 100 + 226 = 7526 \approx 7.53$  kDa.

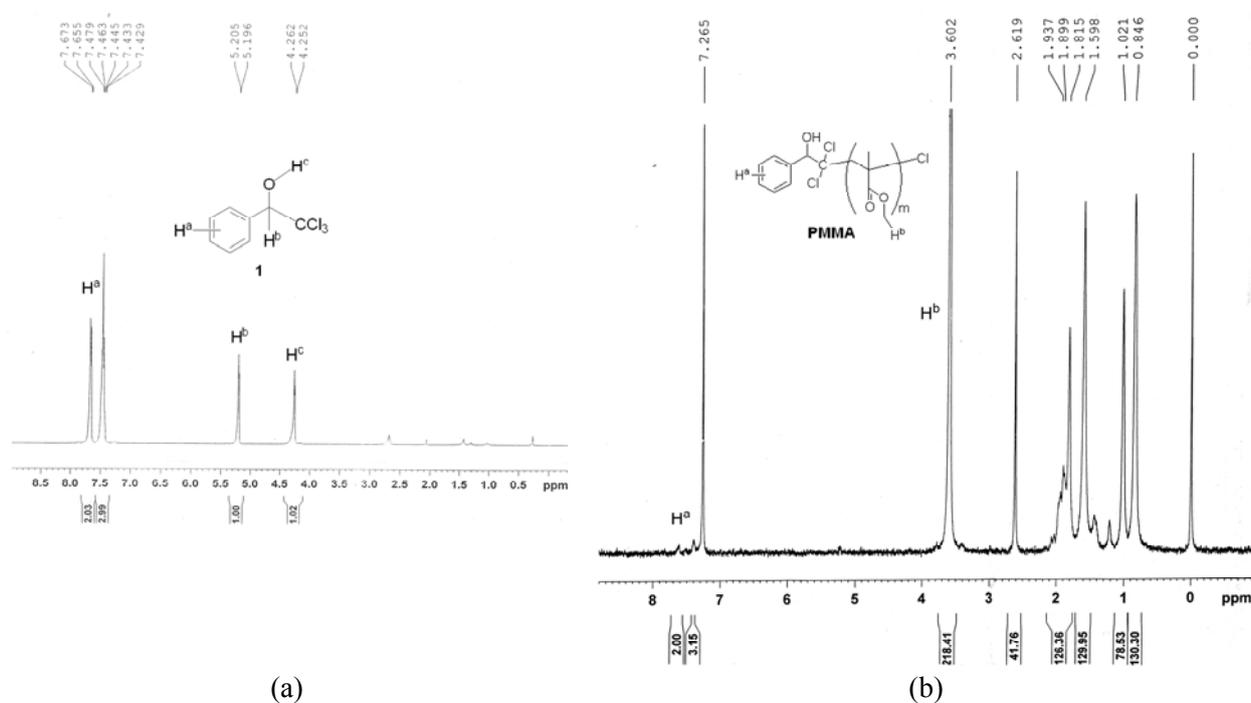
### 3.2. Preparation of PCL catalyzed by $\text{FeCl}_3$

Poly( $\epsilon$ -caprolactone) (PCL) is a useful polymer due to its bio-compatibility, bio-degradability, shape-memory, etc. and has been applied in tissue engineering. Toxic or expensive metal catalysts are usually used in conventional preparation of PCL, which limits its wide use in bio- or medical-related

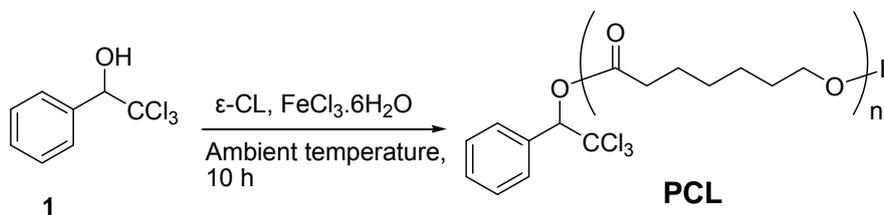
areas. So, production of PCL with non-toxic and cheap catalysts is desirable. In this work, non-toxic and cheap iron(III) chloride as a catalyst is successfully utilized to prepare PCL. The method (Scheme 2) features simplicity and very mild reaction conditions (at ambient temperature).  $^1\text{H}$  NMR spectrum of PCL is demonstrated in Figure 2. Similar to characterization of PMMA, the value of integration of peaks at 7.3-7.7 ppm is five, and that at 4.06 ppm is 154, indicating that there are totally  $154/2 = 77$  of methylene groups close to oxygen (i.e.,  $\text{OCH}_2$ ). So, the number of CL unit is about 77. Molecular mass of PCL can be achieved as:  $128 \times 77 + 226 = 10082 \approx 10.08$  kDa.



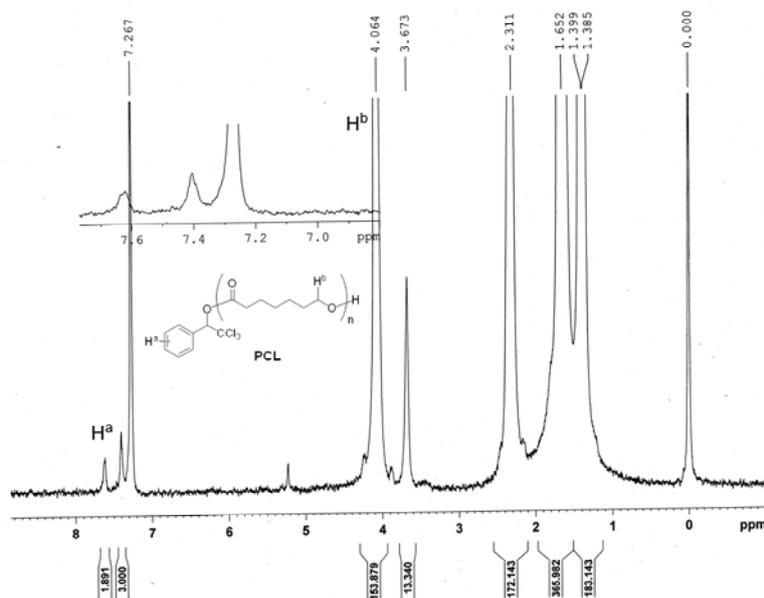
**Scheme 1.** Synthesis of PMMA under AGET ATRP conditions.



**Figure 1.** (a)  $^1\text{H}$  NMR spectrum of the initiator  $\alpha$ -trichloromethyl benzyl alcohol (**1**); (b)  $^1\text{H}$  NMR spectrum of PMMA.



**Scheme 2.** Synthesis of PCL catalyzed by iron(III) chloride.



**Figure 2.** <sup>1</sup>H NMR spectrum of Poly(ε-caprolactone) (PCL).

#### 4. Conclusions

Using the functional molecule  $\alpha$ -trichloromethyl benzyl alcohol as initiators for both AGET ATRP and ROP, the corresponding polymers PMMA and PCL were readily prepared in moderate conversions catalyzed by only one catalyst  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ . The method features mild reaction conditions, simple reaction system, green and cheap catalyst. The prepared polymers PMMA and PCL were characterized by <sup>1</sup>H NMR, and molecular weights were 7.53 kDa and 10.08 kDa, respectively. This approach is expected to prepare PMMA-*b*-PCL block copolymer simultaneously or in one pot, and this work is still under investigation.

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