Single Electron Transfer Living Radical Polymerization via a New Initiator

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Abstract. Research and development of novel initiating system such as single electron transfer living radical polymerization (SET-LRP) is of high importance in polymer chemistry. A new SET-LRP initiator was synthesized and applied to prepare end-functionalized poly(methyl methacrylate) (PMMA) in this study. α-Trichloromethyl benzyl alcohol was firstly synthesized, followed by preparation of PMMA under SET-LRP conditions. Conversion of MMA was 81.9%, and the molecular weight of PMMA was about 2.5 kDa at 60 °C for 1 h. Consistency of the number-average molecular weight of PMMA from NMR, GPC and theoretical calculation indicated that the polymerization featured controllable property. Broad molecular weight distribution (MWD) may be ascribed to branched polymers formed by initiation and chain transfer.

Keyword: Single electron transfer living radical polymerization (SET-LRP); α-Trichloromethyl benzyl alcohol; initiator; poly(methyl methacrylate) (PMMA)

Introduction

Controlled/living radical polymerization methods opened a new door for precise syntheses of polymers or macromolecules with different topological architectures. Among those methods, single electron transfer living radical polymerization (SET-LRP) approach has attracted more and more attention in recent years since its report by Percec and coworkers [1-4]. Various polymers with different topological architectures can be prepared by SET-LRP method. For example, Ding et al. has studied the polymerization of styrene[5], and Chen and his colleagues reported preparation of poly(vinyl acetate) via SET-LRP[6]. SET-LRP has opened a new area of living polymerization, which has advantages such as low catalyst loading, rapid reaction rate, and higher molecular weight of the prepared polymers [7-9].

α-Trichloromethyl benzyl alcohol is an important intermediate of some fragrance and flavor compounds, which can be readily synthesized by cheap benzaldehyde and chloroform in the presence of a strong base. To the best of our knowledge, there is no report on the use of this functional molecule as an initiator of controlled/living radical polymerizations.

1. Experimental

1.1 Instruments and reagents

BrukerAV 400MHz nuclear magnetic resonance meter (CDCl3 as solvent, TMS as internal standard) was used for the experiments.

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Benzenaldehyde, chloroform, tetrabutylammonium bromide (TBAB) and dimethyl sulfoxide (DMSO) were all AR grade and used as received. Methyl methacrylate (MMA) was treated with NaOH to remove possible inhibitor.

1.2 Synthesis of α-trichloromethyl benzyl alcohol

A solution of benzaldehyde (10.6 g, 100 mmol), chloroform (16 mL), acetone (2 mL) and TBAB (2.0 g, 6 mmol) was cooled to 0 oC, followed by adding 50 wt% of aqueous KOH (9 mL). The mixture was stirred at 10 oC for 3 h. Water was added to the mixture, and the organic layer was separated, washed with 5 wt% aqueous HCl, water, dried with anhydrous Na2SO4, and concentrated in vacuo to afford the crude product. Water vapour distillation gave pure product as an oil (17.6 g, 78.1%). 1H NMR (400 MHz, CDCl3): δ 7.58-7.51 (m, 2H), 7.34 -7.30 (m, 3H), 5.15 (s, 1H); 13C NMR (100 MHz, CDCl3): δ 134.9, 129.5, 129.2, 127.8, 103.1, 84.5.

1.3 Preparation of PMMA via SET-LRP

A mixture of MMA (5.0 g, 50 mmol), copper power (0.05 g, 0.2 mmol), α-trichloromethyl benzyl alcohol (0.05 g, 0.2 mmol), and 2,2'-bipyridyl (0.156 g, 1 mmol) in DMSO (10 mL) was stirred at 60 oC for 1 h under N2 atmosphere. Excess cold methanol was added, and the precipitate was filtered to give crude polymer. The crude PMMA was purified by Al2O3 column chromatography to give white product (4.15 g, 81.9%).

2. Results and Discussion

2.1 Characterization of PMMA

Molecular weight and molecular weight distribution (MWD or PDI) are important parameters of polymers. Firstly, PMMA was characterized by 1H NMR spectrum as shown in Figure 1. The peak at lower field corresponded to aryl protons, indicating that the PMMA polymer had a phenyl ring as the end-group, which proved that α-trichloromethyl benzyl alcohol as an initiator had successfully initiated the polymerization of MMA under SET-LRP conditions. The integral area of the peak at 7.4 ppm was designated as 5, as there were 5 protons in the only phenyl ring of the polymer, and integration values of other peaks were based on this peak. At the chemical shift of 3.5 ppm, the integration value was 731, indicating that there were about 731/3 = 244 of methoxy groups in PMMA, i.e. about 244 of MMA units. Thus, the number-average molecular weight of PMMA can be calculated as follows: Mn,NMR = 244 × 100 + 225 = 24625 ≈ 24.6 kDa, where 225 was the molecular weight of the initiator, while 100 was the molecular weight of MMA monomer. The theoretical molecular weight of PMMA was Mn,th = 20.7 kDa when the conversion of MMA monomer was 81.9%. Thus, the molecular weight of PMMA from 1H NMR was consistent with the theoretical one.

Fig. 1 1H NMR spectrum of PMMA
To further characterize the PMMA polymer, GPC was conducted and the diagram is demonstrated in Figure 2. The number-average molecular weight of PMMA measured by GPC was \( M_{n,\text{GPC}} = 23.4 \) kDa. Thus, we have obtained the following data: \( M_{n,\text{th}} = 20.7 \) kDa, \( M_{n,\text{NMR}} = 24.6 \) kDa, \( M_{n,\text{GPC}} = 23.4 \) kDa, and primary consistency of the data indicated that the polymerization featured controlled property. However, molecular weight distribution (MWD) of the PMMA was not ideal, i.e., with a broad value of 1.8. This may be explained as follows: there were three chlorine atoms in the initiator \( \alpha \)-trichloromethyl benzyl alcohol, and branched polymers might be formed during polymerization process.

\[ M_{n,\text{GPC}} = 23.4 \text{ kDa} \]

\[ 15 \ 20 \ 25 \ 30 \]

Time (min)

\[ M_{n,\text{GPC}} = 23.4 \text{ kDa} \]

\[ 0.0 \ 0.2 \ 0.4 \ 0.6 \ 0.8 \]

Conversion (%)

time (min)

\[ 20 \ 40 \ 60 \ 80 \ 100 \]

conversion

\[ \ln([M]/[M]) \]

\[ 0.0 \ 0.2 \ 0.4 \ 0.6 \ 0.8 \ 1.0 \]

Conversion

ln([M]/[M])

time (min)

Fig. 2  GPC diagram of the prepared PMMA

2.2 Effect of temperature on conversion of MMA

As shown in Figure 3, polymerization can undergo at 20 oC with low reaction rate. The conversion was 81.9% when the temperature was increased to 60 oC, and further increasing temperature to 80 oC did not improve the conversion. Therefore, the optimized temperature of the reaction was 60 oC.

\[ \begin{align*}
\text{Conversion (\%)} \\
\text{temperature (\degree C)}
\end{align*} \]

2.3 Effect of time on conversion of MMA

At 60 oC, the influence of time on the conversion of MMA was determined as demonstrated in Figure 4. The conversion was gradually improved with the increase of reaction time, and when the time was 60 min, the conversion was 81.9%. Longer reaction time has no evident positive effect on the conversion, so 60 min was the optimal reaction time. Kinetic curve of \( \ln([M]/[M]) \) vs. time showed that linear relationship between \( \ln([M]/[M]) \) and reaction time conforming to first-order reaction kinetics.

3. Conclusions

The functional molecule \( \alpha \)-trichloromethyl benzyl alcohol was used as a SET-LRP initiator for the first
time to polymerize MMA. The conversion of MMA was 81.9% under optimized conditions: time of 1 h, and temperature of 60 oC. The benzyl alcohol-ended PMMA product is expected to further undergo opening polymerization to prepare biocompatible block copolymers [10-11], and the related work is still underway.

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