

## Synthesis of star polymethyl acrylate by SET-LRP at ambient temperature

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**Abstract** The star-shaped polymethyl acrylate (PMA) was synthesized by single electron transfer living radical polymerization (SET-LRP) at 30 °C in dimethyl sulfoxide, using 2,2-dibromomethyl-1,3-dibromopropane as the multifunctional initiator, Cu<sup>0</sup> powder and tris-(2-dimethylamino ethyl)amine (Me<sub>6</sub>-TREN) as catalyst. The structure of polymer was analyzed by <sup>1</sup>H NMR, and the results showed that the star-shaped PMA had perfect chain ends (–Br) retention. In addition, the polymerization proceeded smoothly and the time dependence of ln([M]<sub>0</sub>/[M]) was linear, which could indicate a first order propagation rate with respect to both radicals and monomer concentration, the polymerization was the living polymerization. The  $M_n$  and  $M_w/M_n$  of polymer were being measured by Gel Permeation Chromatography. The  $k_p^{app} = 0.0367 \text{ h}^{-1}$  and the conversion was 36.3% at 16 h, meanwhile the  $M_n^{GPC}$  of the polymer was 13,300 and the  $M_w/M_n$  was 1.40.

**Keywords** Single electron transfer living radical polymerization · Star polymer · Methyl acrylate

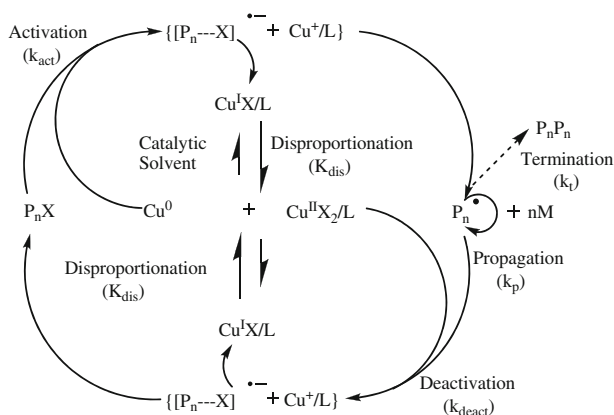
### Introduction

Living radical polymerization is an important way to achieve molecular design, synthesis of polymers with the exact primary structure, and to control the molecular weight and molecular distribution, but all the traditional living radical polymerizations have shortcomings [1–3]. Single electron transfer living radical

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**Scheme 1** Mechanism of SET-LRP; X = Cl, Br, I; L = nitrogen-based ligand

polymerization (SET-LRP) [4] is a novel polymerization at low reaction temperature, using less catalyst, with ultra-high polymerization rate and colorless product, so far it has been the better polymerization. Scheme 1 [5] shows the proposed mechanism of SET-LRP. SET-LRP has been successfully applied in synthesis of poly(acrylate)s [4, 6–9], poly(methacrylate)s [4, 10–12], poly(vinyl chloride) [4, 13, 14], and poly(acryl amide)s [15, 16] under mild reaction conditions, but mostly the products are linear polymers or bifunctional polymers even using some trifunctional initiator such as  $\text{CHI}_3$ ,  $\text{CHBr}_3$ , and  $\text{CHCl}_3$  [9, 17]. Compared with the linear polymer with the same molecular weight, the star polymer has lower crystallinity, lower diffusion coefficient, lower melt viscosity, and hydrodynamic volume; therefore it was widely used in industrial and medical fields [18–20]. The star polymer being prepared by SET-LRP is rare, particularly using the multifunctional initiator which is similar to  $\text{CHCl}_3$ ,  $\text{CHBr}_3$ , or  $\text{CHI}_3$ . In this study, the star polymethyl acrylate prepared by SET-LRP at low temperature in Dimethyl Sulfoxide (DMSO) is reported, with using 2,2-dibromomethyl-1,3-dibromopropane ( $\text{PEBr}_4$ ) as initiator and  $\text{Cu}^0$  powder/tris-(2-dimethylamino ethyl)amine ( $\text{Me}_6\text{-TREN}$ ) as catalytic system.

## Experimental

### Materials

Methyl acrylate (MA, >99.0%, Sinopharm Chemical Reagent Co., Ltd., China) was passed through a basic  $\text{Al}_2\text{O}_3$  chromatographic column, and the monomer was washed with the aqueous solution of NaOH (5 wt%), followed by washed with deionized water until the solution was neutralized. The resulting solution was dried overnight by anhydrous sodium sulfate, distilled at reduced pressure, and stored below 0 °C. Tris(2-aminoethyl)amine (TREN, 96%, Acros),  $\text{Cu}^0$  powder (75  $\mu\text{m}$ , 99%, Aldrich) were used as received. All other chemicals were purchased from

Sinopharm Chemical Reagent Co., Ltd., and were used as received unless mentioned. Tris-(2-dimethylamino ethyl) amine and 2,2-dibromomethyl-1,3-dibromopropane were synthesized as described in the literature[21] and [22], respectively.

### Characterization

The  $^1\text{H}$  NMR spectrum of purified polymer was recorded on a Bruker DRX 500 MHz nuclear magnetic resonance instrument at 30 °C with  $\text{CDCl}_3$  as solvent and tetramethylsilane was being used as internal standard. The number average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of the polymers being prepared via SET-LRP were determined using a Waters 1515 Gel permeation chromatography (GPC) being equipped with a refractive-index detectors, using 100 Å, 5  $\mu\text{m}$ ; 500 Å, 5  $\mu\text{m}$ ; and 10,000 Å, 5  $\mu\text{m}$  columns with molecular weights ranging from  $10^2$  to  $10^5$  g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min at 30 °C.

Typical procedures for polymerization kinetics SET-LRP of MA initiated with  $\text{PEBr}_4$

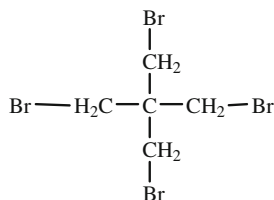
The monomer (MA, 20.00 mL, 0.22 mol), solvent (DMSO, 10 mL), initiator ( $\text{PEBr}_4$ , 0.2143 g, 0.55 mmol), and catalyst ( $\text{Cu}^0$  powder, 0.0142 g, 0.22 mmol) were added into 100-mL ampoule being equipped with an magnetic needle in following order:  $\text{Cu}^0$  powder, monomer, initiator, and solvent. Then, the solution was deoxygenated with six standard freeze-pump-thaw-filling nitrogen cycles, and the ligand ( $\text{Me}_6\text{-TREN}$ , 64.0  $\mu\text{L}$ , 0.22 mmol) was added to the mixture under nitrogen protection. The ampoule was sealed and placed in a stirred water bath under 30  $\pm$  0.1 °C. Up to the desired polymerization time, the ampoule was cooled by liquid nitrogen, and the mixture was precipitated into 300 mL cool methanol with stirring strongly. The product was dissolved in acetone and passed through a basic neutral  $\text{Al}_2\text{O}_3$  column to remove the unreacted  $\text{Cu}^0$  powder and  $\text{Cu}^{\text{II}}$  compound. The resulting solution was precipitated in 300 mL of cold methanol; the polymer was isolated by filtration and dried under vacuum until a constant weight. The monomer conversion was determined by gravities, the samples were dissolved in  $\text{CDCl}_3$  for detection by  $^1\text{H}$  NMR spectroscopy, and also the samples were dissolved in DMF for GPC analysis, the  $M_n$  and  $M_w/M_n$  values were determined by GPC with PMMA standards.

## Results and discussions

### Characterization of $\text{PEBr}_4$

Scheme 2 shows the structure of  $\text{PEBr}_4$ , and its melting point is 162.5–162.8 °C (163 °C, literature [22]), in the infrared spectra (KBr), the  $-\text{OH}$  absorption peak around 3300  $\text{cm}^{-1}$  disappears, and around 601  $\text{cm}^{-1}$  is the absorption peak of the

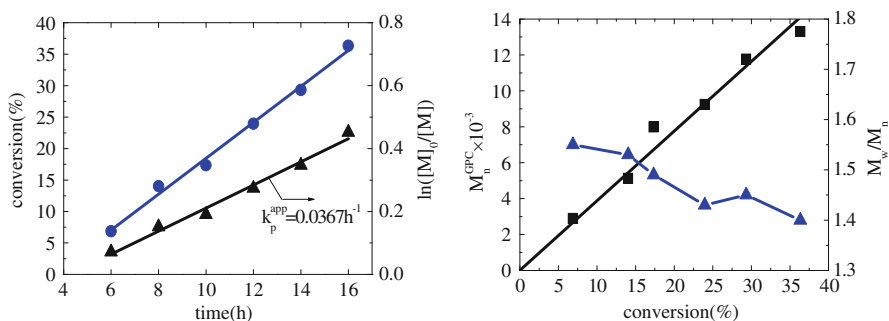
**Scheme 2** The structure of  $\text{PEBr}_4$



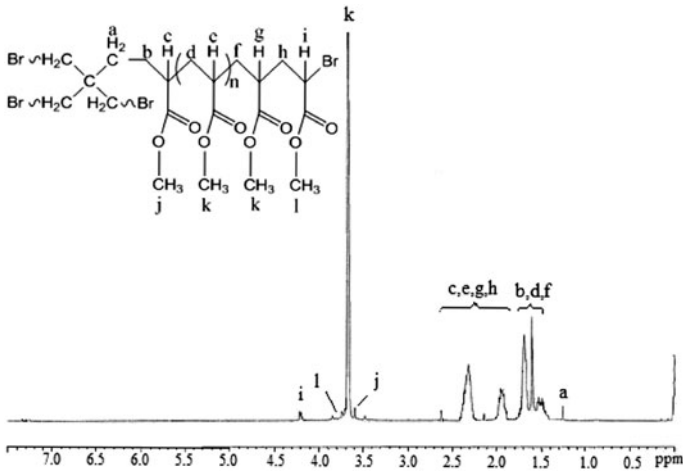
$\text{C}-\text{Br}$ ,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 3.589$  ppm (s, 8H) is the proton signal peak of  $-\text{CH}_2\text{Br}$ .

### SET-LRP of MA in DMSO

The  $\text{Cu}^0$  powder/ $\text{Me}_6\text{-TREN}$  catalyzed SET-LRP of MA was carried out at  $30^\circ\text{C}$  in DMSO using the  $\text{PEBr}_4$  as multifunctional initiator. The reaction conditions were as follows:  $[\text{MA}]_0/[\text{PEBr}_4]_0/[\text{Cu}^0 \text{ powder}]_0/[\text{Me}_6\text{-TREN}]_0 = 200/0.5/0.2/0.2$ ,  $[\text{MA}]_0 = 7.4$  mol/L.  $\text{Cu}^0$  powder with a particle size of  $75\ \mu\text{m}$  was being used as primary activator. Figure 1 presented the kinetic plots of polymerization. The value of the apparent rate constant of propagation ( $k_p^{\text{app}}$ ) was shown on the kinetic plots. The time dependence of  $\ln([\text{M}]_0/[\text{M}])$  increased linearly, which indicated a first order propagation rate respect to both radical and monomer concentrations and that the concentration of radical was constant during the polymerization. Moreover, the polymer with narrow distribution was obtained ( $k_p^{\text{app}} = 0.0367\ \text{h}^{-1}$ ,  $M_n^{\text{GPC}} = 13300$ ,  $M_w/M_n = 1.40$ , 36.3% conversion in 16 h) and the number average molecular weight of PMA ( $M_n^{\text{GPC}}$ ) followed a linear dependence on the conversion and was almost close to the theoretical molecular weight ( $M_n^{\text{th}}$ ). It should be noted that there is an induction period of about 4 h in DMSO, the value of  $k_p^{\text{app}}$  was low, that may be caused by the steric hindrance effect of initiator and the low diproportionation constant rate of  $\text{Cu}^{\text{I}}\text{X/L}$  in DMSO [23, 24]. All these suggest the polymerization was a living radical polymerization.



**Fig. 1** Kinetic plots for the  $\text{Cu}^0/\text{Me}_6\text{-TREN}$  catalyzed SET-LRP of MA initiated with  $\text{PEBr}_4$  at  $30^\circ\text{C}$  in DMSO. Reaction conditions:  $[\text{MA}]_0/[\text{PEBr}_4]_0/[\text{Cu}^0 \text{ powder}]_0/[\text{Me}_6\text{-TREN}]_0 = 200/0.5/0.2/0.2$ ,  $[\text{MA}]_0 = 7.4$  mol/L, MA = 20.00 mL, DMSO = 10 mL,  $\text{Cu}^0 = 75\ \mu\text{m}$  powder.  $[\text{M}]_0$  refers to the initial concentration of MA and  $[\text{M}]$  refers to the instant concentration of MA



**Fig. 2** 400 MHz  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of star PMA,  $M_n^{\text{GPC}} = 13300$ ,  $M_w/M_n = 1.40$  obtained at 36.3% conversion

### Characterization of star polymethyl acrylate

Figure 2 showed the  $^1\text{H}$  NMR of the polymer obtained at 36.3% conversion,  $M_n^{\text{GPC}} = 13300$ ,  $M_w/M_n = 1.40$ . The proton signal of the H(a) appeared at  $\delta = 1.254$  ppm, the protons signals of the main chain ( $-\text{CH}_2-$  and  $-\text{CH}-$ , H(b–h)) were presented in the region  $\delta = 1.436$ – $2.623$  ppm. The signal of  $-\text{OCH}_3$  side groups (H(j), H(k), and H(l)) appeared in the region  $\delta = 3.614$ – $3.714$  ppm. Because of the signal of the proton  $-\text{CH}-$  located in the  $\alpha$ -position of the bromine chain end (H(i)) was affected by  $-\text{Br}$ , the chemical shift moved to high field,  $\delta = 4.196$  ppm is the signal of proton of H(i). In addition, the signal of proton of  $-\text{CH}_2\text{Br}$  for the initiator disappeared and only did the signal of proton H(i) appear, which could indicate the polymer prepared by SET-LRP was star polymer and the polymerization was living radical polymerization.

### Conclusion

In summary, the four-arm star-shaped polymethyl acrylate was synthesized by SET-LRP with  $\text{PEBr}_4$  as multifunctional initiator and  $\text{Cu}^0$  powder/ $\text{Me}_6\text{-TREN}$  as catalytic system in DMSO under mild reaction condition. Under this condition, the polymers with relative narrow polydispersity were obtained ( $M_n^{\text{GPC}} = 13300$ ,  $M_w/M_n = 1.40$ , obtained at 36.3% conversion in 16 h), and the polymers had perfect chain ends  $-\text{Br}$  retention, moreover, the kinetics plot of polymerization under this condition was first order. All these suggested the multifunctional initiators similar to  $\text{PEBr}_4$  were efficient for synthesizing the star polymers by SET-LRP at mild condition, and this provided a new way to synthesize star polymers.

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