

Preparation of hyperbranched polymer via single electron transfer living radical polymerization

X Zhang, X H Chen, J Li, X X Cao and C J Cheng¹

School of Chemistry and Chemical Engineering, Jiangxi Science & Technology Normal University, Nanchang, Jiangxi, 330013, P.R. China

E-mail: chengcj530@163.com

Abstract. α -Trichloromethyl benzyl alcohol is converted to α -trichloromethyl benzyl methacrylate in 62% yield under esterification conditions. The ester proves to be a good inimer to prepare hyperbranched polymer by utilizing SET-LRP approach. The monomer conversion is about 72% at 60°C for 6 h.

1. Introduction

Hyperbranched polymers have attracted wide attention in recent years due to their unique architectures with dense end groups on their periphery. Compared with their linear counterparts, the outstanding structures of these kinds of polymers result in outstanding properties: soluble in solvents though they are highly branched; low viscosity in solution due to their compact shape [1-3]. Therefore, the polymers have found a variety of practical or potential applications in many fields such as coatings [4], drug delivery [5, 6], optical and electrical polymers [1], etc. Synthesis of hyperbranched polymers usually involves three methods: one is copolymerization of commercially available mono-vinyl monomers with small amount of bi- or multi-vinyl monomers; the second is polymerization of bi- or multi-vinyl monomers in the presence of excess initiator, which can guarantee low molecular weight of the polymers and avoid crosslinking by controlling feedstocks; the third is self-condensing vinyl polymerization via use of a species called inimer [7].

Single electron transfer living radical polymerization (SET-LRP) is one of living radical polymerization approaches developed by Percec and coworkers [8-10]. In comparison with other methods, SET-LRP shows some unique advantages such as mild reaction conditions, rapid polymerization rate, low catalyst loading, and high molecular mass of the polymer products [11].

α -Trichloromethyl benzyl alcohol is a functional small molecule, which can be easily synthesized by dichloro-carbene method. This molecule has been successfully used as an initiator of SET-LRP reactions in our previous work [12]. Herein, as a continuation of our previous work, an inimer is synthesized from α -trichloromethyl benzyl alcohol and further utilized to prepare hyperbranched polymer.

2. Experimental

¹ Address for correspondence: C J Cheng, School of Chemistry and Chemical Engineering, Jiangxi Science & Technology Normal University, Nanchang, Jiangxi, 330013, P.R. China. E-mail: chengcj530@163.com.



2.1. Reagents and instruments

NMR spectra were measured by BrukerAV 400MHz nuclear magnetic resonance meter.

Benzaldehyde, chloroform, tetrabutylammonium bromide (TBAB), methacryloyl chloride, triethyl amine (TEA), dichloromethane, petroleum ether (PE), ethyl acetate (EA), dimethyl sulfoxide (DMSO), and 2, 2'-bipyridyl (BPY) were all AR grade purity and used as received. Before use, aqueous sodium hydroxide was utilized to treat methyl methacrylate (MMA) to remove possible inhibitor.

2.2. Synthesis of methacrylate ester (2) of α -trichloromethyl benzyl alcohol

Compound 1 was synthesized in moderate yield from benzaldehyde and chloroform according to literature [12]. Compound 1 (6.77 g, 30 mmol) and triethyl amine (6.07 g, 60 mmol) were dissolved in dichloromethane (30 mL), and the resulting solution was cooled to -5°C . Then, methacryloyl chloride (2.09 g, 20 mmol) in dichloromethane (10 mL) was added dropwise. After the addition was completed, the mixture was stirred at -5°C for 12 h. The solid was removed by filtration, and the filtrate was washed with water, saturated Na_2CO_3 , and brine, dried with anhydrous sodium sulfate. After concentrated in vacuo, the crude product was purified on silica gel chromatography using PE/EA (10:1, v : v) as the eluant to give an oily product 2 (3.64 g, 62%). ^1H NMR (400 MHz, CDCl_3): δ 7.68-7.65 (m, 2H), 7.45-7.38 (m, 3H), 6.44 (s, 1H), 6.38 (s, 1H), 5.75-5.74 (m, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 164.9, 135.3, 133.2, 129.8, 129.6, 128.0, 99.5, 83.5, 83.2, 82.7, 82.3, 18.2.

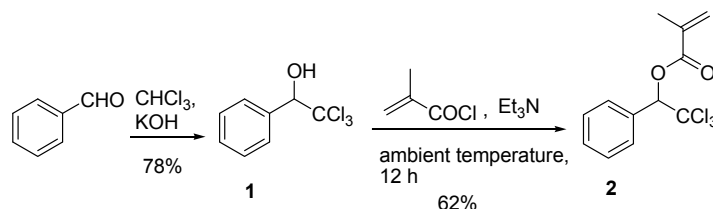
2.3. Preparation of hyperbranched polymer by using MMA and the inimer (2)

To a flask were added copper power (0.05 g, 0.2 mmol), MMA (5.0 g, 50 mmol), 2, 2'-bipyridyl (0.156 g, 1 mmol), α -trichloromethyl benzyl methacrylate (2) (1.48 g, 5 mmol), and DMSO (10 mL). The mixture was stirred at 60°C for 6 h under N_2 atmosphere. Crude hyperbranched polymer was given by precipitation and subsequent filtration. Further purification on neutral Al_2O_3 column chromatography gives a white solid. $M_{n,\text{GPC}} = 90$ kDa, PDI = 1.25.

3. Results and discussion

3.1. Synthesis and characterization of the inimer α -trichloromethyl benzyl methacrylate (2)

It is known that multi-halo-compounds such as CHCl_3 , CCl_4 , CHBr_3 can be used as an atom transfer radical polymerization (ATRP) or SET-LRP initiator [13]. Our previous work proved that α -trichloromethyl benzyl alcohol (1) can also be a SET-LRP initiator as its structure was similar to chloroform. Thus, compound 1 can further react with methacryloyl chloride to form α -trichloromethyl benzyl methacrylate (2) (scheme 1). As the reactant methacryloyl chloride and the product 2 are all very reactive, the reaction must be conducted at low temperature to avoid some side reactions such addition or polymerization.



Scheme 1. Synthesis of the inimer α -trichloromethyl benzyl methacrylate (2).

^1H NMR and ^{13}C NMR spectra of the inimer α -trichloromethyl benzyl methacrylate (2) were shown in figure 1, together with those of α -trichloromethyl benzyl alcohol (1) for comparison.

3.2. Preparation of hyperbranched polymer from the inimer α -trichloromethyl benzyl methacrylate (2)

In the compound α -trichloromethyl benzyl methacrylate (2), the trichloromethyl group can be SET-LRP initiator, and methacryloyl group be polymeric monomer. Therefore, compound 2 is able to be an inimer. Thus, with $\text{Cu}(0)$ as the catalyst, BPY as the ligand, DMSO as the solvent, the hyperbranched

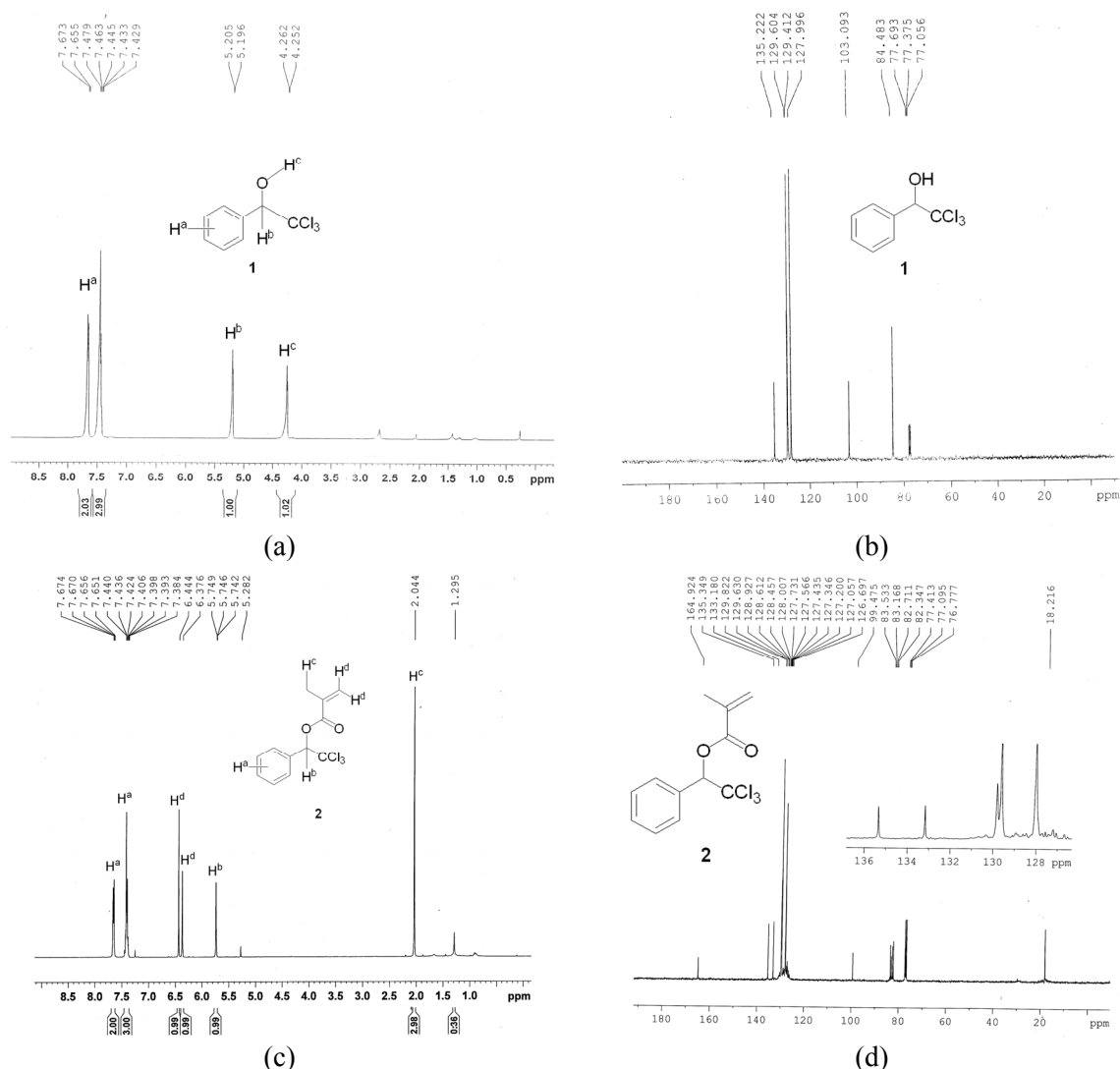
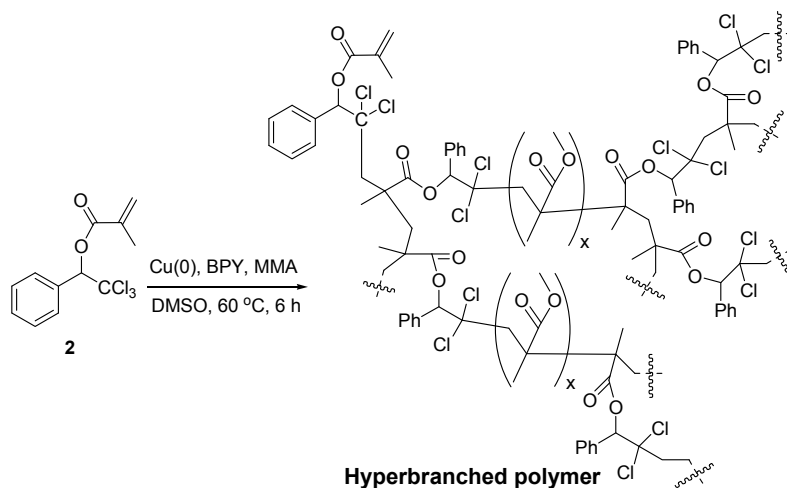


Figure 1. (A) ^1H NMR spectrum of α -trichloromethyl benzyl alcohol (1); (B) ^{13}C NMR spectrum of α -trichloromethyl benzyl alcohol (1); (C) ^1H NMR spectrum of the inimer α -trichloromethyl benzyl methacrylate (2); (D) ^{13}C NMR spectrum of the inimer α -trichloromethyl benzyl methacrylate (2).



Scheme 2. Preparation of hyperbranched polymer by SET-LRP.

polymer is prepared under SET-LRP conditions (scheme 2). Under the conditions, i.e., at 60°C for 6 h, the hyperbranched polymer is easily obtained, with monomers conversion of about 72%. Further optimization of the reaction conditions is still underway.

4. Conclusions

A new inimer α -trichloromethyl benzyl methacrylate is designed and synthesized in 62% yield from α -trichloromethyl benzyl alcohol. The intermediate and the inimer are well characterized by NMR spectra. The inimer is then self-polymerized under SET-LRP conditions to form the desired hyperbranched polymer. The polymer is characterized by GPC to obtain M_n of about 90 kDa, PDI = 1.25. Further studies on the characterization of the polymer by NMR, DSC, viscosity is under further investigation.

Acknowledgment

The authors acknowledge financial support from the Natural Science Foundation of China (No. 21264008) and the 8th Foundation of Creativity and Study for College Students in Jiangxi Science Technology Normal University.

References

- [1] Wu W B, Tang R L, Li Q Q and Li Z 2015 Functional hyperbranched polymers with advanced optical, electrical and magnetic properties *Chem. Soc. Rev.* (in press)
- [2] Hult A, Johansson M and Malmström E 1999 Hyperbranched polymers *Adv. Polym. Sci.* **143** 1-34
- [3] Rikkou-Kalourkoti M, Matyjaszewski K and Patrickios C S 2012 Synthesis, characterization and thermolysis of hyperbranched homo- and amphiphilic co-polymers prepared using an inimer bearing a thermolyzable acylal group *Macromolecules* **45** 1313-20
- [4] Mehta P N 2006 Hyperbranched polymers: Unique design tool for coatings *Surface Coatings International Part B: Coatings Transactions* **89** 333-42
- [5] Paleos C M, Tsiourvas D, Sideratou Z and Tziveleka L A 2010 Drug delivery using multifunctional dendrimers and hyperbranched polymers *Expert Opin Drug Deliv.* **7** 1387-98
- [6] Zill A, Rutz A L, Kohman R E, Alkilany A M, Murphy C J, Kong H and Zimmerman S C 2011 Clickable polyglycerol hyperbranched polymers and their application to gold nanoparticles and acid-labile nanocarriers *Chem. Commun.* **47** 1279-81
- [7] Tsarevsky N V, Huang J Y and Matyjaszewski K 2009 Synthesis of hyperbranched degradable polymers by atom transfer radical (co) polymerization of inimers with ester or disulfide groups *J. Polym. Sci. A: Polym. Chem.* **47** 6839-51
- [8] Percec V, Guliashvili T, Popov A V and Ramirez-Castillo E 2005 Catalytic effect of dimethyl sulfoxide in the Cu(0)/ tris (2-dimethylaminoethyl) amine-catalyzed living radical polymerization of methyl methacrylate at 0–90°C initiated with CH₃CHCl₂ as a model compound for α , ω -di (iodo) poly (vinyl chloride) chain ends *J. Polym. Sci. A: Polym. Chem.* **43** 1935-47
- [9] Levere M E, Nguyen N H, Leng X F and Percec V 2013 Visualization of the crucial step in SET-LRP *Polym. Chem.* **4** 1635-47
- [10] Zhang Q, Zhang Z B, Wang W X, Cheng Z P, Zhu J, Zhou N C, Zhang W, Wu Z Q and Zhu X L 2011 In Situ Cu(0) Catalyzed SET-LRP: The first attempt *J. Polym. Sci. A: Polym. Chem.* **49** 4694–700
- [11] Lu G L, Li Y J, Guo H, Du W Y and Huang X Y 2013 SET-LRP synthesis of novel polyallene-based well-defined amphiphilic graft copolymers in acetone *Polym. Chem.* **4** 3132-9
- [12] Bai X X, Hu Y, Zhang X, Ai L L and Cheng C J 2014 Single electron transfer living radical polymerization via a new initiator *IOP Conf. Series: Materials Science and Engineering* **62** 012008

- [13] Matyjaszewski K and Xia J H 2001 Atom transfer radical polymerization *Chem. Rev.* **101** 2921-90