



# Synthesis of 4-arms hydroxy-functionalized PMMA-b-PE through combining free radical polymerization with coordination polymerization



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## ABSTRACT

The copolymerization of MMA with ethylene was promoted by metallocene complex in the presence of initiator tetra(2,3-epoxy propoxy)silane ( $I_s$ ), reducing agent Zn and cocatalyst MAO, combining free radical polymerization with coordination polymerization via sequential monomer addition strategy in one-pot to produce 4-arms hydroxy-functionalized PMMA-b-PE. The effects of polymerization conditions such as temperature, time, ethylene pressure and Al/Ti molar ratio on the polymerization performance were investigated. 4-Arms hydroxy-functionalized PMMA-b-PE was obtained by solvent extraction and determined by GPC, MALLS, DSC, FT-IR, WAXD and  $^1\text{H}$  ( $^{13}\text{C}$ ) NMR. The DSC result indicated that the 4-arms hydroxy-functionalized PMMA-b-PE had one  $T_g$  at 87.0 °C and one  $T_m$  at 117.0 °C which attributed to  $T_g$  of PMMA segment and  $T_m$  of PE segment, respectively. The microstructure of 4-arms hydroxy-functionalized PMMA-b-PE was further confirmed by WAXD, FT-IR, and  $^{13}\text{C}$  NMR analysis. These results demonstrated that the obtained 4-arms block copolymer consisted of PMMA segment and crystalline PE segment.

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## 1. Introduction

Recent decades, multi-arms polymers have received great attention due to their impressive viscoelastic behavior, mechanical properties, and compatibilities with other polymeric materials. Y-shaped hydrophilic block copolymers were synthesized via functional atom transfer radical polymerization (ATRP) macro-initiators [1,2]. Milktoarm and homoarm star copolymers were synthesized by arm-first method as a simple and general method following living free radical principle [3]. The functionalized asymmetric star polymers containing conductive polyacetylene segments were built by living anionic polymerization [4]. Takaho et al. [5] reported that quantitative synthesis of star-shaped poly(vinyl ether)s with a narrow molecular weight distribution were synthesized by living cationic polymerization. By “core-first” strategy, three-arm star polyethylene was formed via ethylene living polymerization promoted with a trinuclear Pd diimine

catalyst following the coordination polymerization mechanism [6]. Living radical polymerization of styrene promoted by metallocene/epoxide/metal catalyst system was investigated by Asandei et al. [7]. He described the polymerization mechanism and the role of each component of the catalyst system for the polymerization. Metallocene complex was reduced by metals to form metallocene complex radical. Subsequent opening of the epoxide ring by metallocene complex radical gave a carbon-centered free radical which initiated the propagation of the monomers. The metallocene complex radical reversibly terminated the growing chain as persistent radical (dormant species) and the number-average molecular weight ( $M_n$ ) and the molecular weight distribution (MWD) of the obtained polymer could thus be controlled. In our previous work [8], the copolymerization of styrene with ethylene was promoted by  $\text{Cp}_2\text{TiCl}_2/\text{I}_n/\text{Zn}/\text{MAO}$  catalyst system combining free radical polymerization with coordination polymerization via sequential monomer addition strategy in one-pot. Herein, we introduced the synthesis of the 4-arms hydroxy-functionalized PMMA-b-PE copolymer catalyzed by  $\text{Cp}_2\text{TiCl}_2/\text{tetra}(2,3\text{-epoxy propoxy)silane}$  ( $I_s$ )/Zn/MAO combining living radical polymerization with coordination polymerization. The effects of conditions

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such as temperature, time, pressure of ethylene, Al/Ti molar ratio on the polymerization performance were investigated.

## 2. Experimental

### 2.1. General procedures and materials

Polymerization-grade ethylene was no further purified; MMA was dried over 5 Å molecular sieve for 8 days, distilled under reduced pressure, and stored under argon atmosphere in a freezer at  $-10\text{ }^{\circ}\text{C}$ ; toluene was refluxed over metallic sodium/benzophenone for 48 h and distilled under a nitrogen atmosphere before use; Dicyclopentadiene and *n*-butyl lithium (1.5 M solution in hexane) were purchased from Acros in China;  $\text{TiCl}_4$ , dichloromethane, chloroform, Zn powder were purchased from Beijing Chemical Agency at Daxing District; Methylalumoxane (MAO) was purchased from Albemarle with 10 wt% solution in toluene.

### 2.2. Synthetic procedure of metallocene complex and $I_s$

$\text{Cp}_2\text{TiCl}_2$  was prepared according to the literature [9] by adding the stoichiometric amount of dicyclopentadiene to an organolithium reagent followed by the reaction with  $\text{TiCl}_4$  in tetrahydrofuran. Elemental analysis for Calcd for  $\text{Cp}_2\text{TiCl}_2$  (249, yield: 74.6%): C, 48.3; H, 4.02; Ti, 19.2; Cl, 28.5. Found: C, 48.3; H, 4.08; Ti, 19.6; Cl, 27.9.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm), 6.46 (s, 10H,  $\text{C}_{10}\text{H}_{10}$ ).

Tetra(2,3-epoxy propoxy)silane ( $I_s$ ): In 300 mL flamed Schlenk flask under nitrogen atmosphere, 150 mL THF as solvent, 5.0 mL  $\text{SiCl}_4$  (0.044 mol), 11.5 mL glycidol (0.176 mol) and triethylamine (0.176 mol) were added in order. The reaction was processed at  $30\text{ }^{\circ}\text{C}$  for 10 h. The mixture was filtrated at r.t. The solvent was removed by vacuum. Tetra(2,3-epoxy propoxy)silane ( $I_s$ ) was obtained, colorless liquid, yield: 65.2%.

Anal. Calcd for  $\text{Si}(\text{C}_3\text{H}_5\text{O}_2)_4$  (FM: 320, bp:  $346.1\text{ }^{\circ}\text{C}$ ): C, 45.0; H, 6.25. Found: C, 45.8; H, 6.30.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm), 2.67–2.80 (m, 2H), 3.14 (m, 1H), 3.50–3.82 (m, 2H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ), three signals at  $\delta$  37.1, 43.6 and 63.3 ppm were observed.

### 2.3. Synthesis of 4-arms hydroxy-functionalized PMMA-*b*-PE

Calculated amount of metallocene complex  $\text{Cp}_2\text{TiCl}_2$  (0.04 g, 0.18 mmol), Zn (0.018 g, 0.27 mmol) and solvent (1,4-dioxane, 10 mL) were added into a 500 mL glass reactor which was degassed and was filled with argon.

All operations were carried out by rigorous repellency of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold line under argon atmosphere. Catalytic precursor ( $\text{Cp}_2\text{TiCl}_2$ ), reducing agent (Zn) in desired molar ratio and 10 mL freshly distilled 1,4-dioxane, were added into the glass reactor which was degassed by several freeze–pump–thaw cycles and filled with argon. The reduction was carried out at room temperature and the characteristic lime-green color of Ti(III) was observed in 5 min. The reactor was then cooled to  $-78\text{ }^{\circ}\text{C}$  by liquid nitrogen. A mixture of MMA and initiator ( $I_s$ ) in desired molar ratio was added under argon. The reactor was degassed and placed into an oil bath at pre-determined temperature. After the reduction occurred in less than 5 min at r.t., a mixture of tetra(2,3-epoxy propoxy)silane ( $I_s$ , 0.05 mL, 0.045 mmol) and monomer (MMA, 3 mL) was injected into the reactor by an air-tight syringe. The reactor was heated up to  $90\text{ }^{\circ}\text{C}$  and stirred for 2.5 h [10]. Then cooled to  $50\text{ }^{\circ}\text{C}$ , 70 mL of toluene and 31.5 mL of MAO (10 wt% in toluene, ratio of Al/Ti was 300 in mol) was introduced and the mixture was stirred for 10 min. Ethylene with desired pressure was charged in and stirred to desired time. The polymerization was terminated by excess amount of methanol/HCl (100/10 in v/v) solution. The resultant

copolymer was filtered and washed with fresh methanol and water, dried by vacuum at  $50\text{ }^{\circ}\text{C}$ . The samples were taken under argon using an airtight syringe for the measurement of  $^1\text{H NMR}$  and  $^{13}\text{C NMR}$  and the measurements of  $M_n$  and MWD after passing an  $\text{Al}_2\text{O}_3$  column.

### 2.4. Solvent extraction

Selective solvent fraction to remove homopolymer was carried out using a Soxhlet extractor. The crude product was placed in a cellulose thimble and extracted successively with boiling THF for 12 h to remove the soluble PMMA. The residue was extracted with boiling  $\text{CHCl}_3$  for 12 h to remove the insoluble homopolyethylene [11]. The  $\text{CHCl}_3$ -soluble fraction (PMMA-*b*-PE) was isolated by evaporation of solvent, dried under vacuum at  $50\text{ }^{\circ}\text{C}$ , weighted, and analyzed by DSC, WAXD, GPC, FT-IR, and  $^{13}\text{C NMR}$  spectroscopy.

### 2.5. Characterization

GPC analysis was performed at  $150\text{ }^{\circ}\text{C}$  on a PL-GPC200, using trichlorobenzene as eluent, linear polystyrene as standard. The glass transition temperature and melting temperature were determined with a Perkin-Elmer DSC-2 system at  $10\text{ }^{\circ}\text{C}/\text{min}$ . Any thermal history difference for the polymers was eliminated by first heating the specimen to  $200\text{ }^{\circ}\text{C}$  for 5 min, cooling at  $10\text{ }^{\circ}\text{C}/\text{min}$  to room temperature then recording the second DSC scan with  $10\text{ }^{\circ}\text{C}/\text{min}$ . WAXD was recorded with a Ricon D/Max-3A diffraction system. The radiation source was nickel filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5405 \times 10^{-10}\text{ m}$ ). The samples were scanned over a  $2\theta$  range from  $5^{\circ}$  to  $40^{\circ}$  at a scan rate of  $0.02^{\circ}/\text{s}$ . FT-IR spectra were recorded by a Nicolet 5DXC FT-IR spectrograph. The spectra were obtained at a  $40\text{ cm}^{-1}$  resolution, and average data were obtained from at least 32 scans in the standard wave number range from 500 to  $4000\text{ cm}^{-1}$ .  $^{13}\text{C NMR}$  and  $^1\text{H NMR}$  (125 MHz for  $^{13}\text{C NMR}$ , TMS as internal standard) spectra were recorded on an INOVA500 spectrometer at  $150\text{ }^{\circ}\text{C}$  in *o*-dichlorobenzene ( $d_4$ ).

## 3. Results and discussion

The course of the MMA/ethylene copolymerization catalyzed by  $\text{Cp}_2\text{TiCl}_2/I_s/\text{Zn}/\text{MAO}$  catalyst system was described in Scheme 1. The initiating radicals (Eq. (2)) were generated from a redox reaction of  $I_s$  with  $\text{Cp}_2\text{Ti(III)Cl}$  which was formed by the room temperature Zn reduction of  $\text{Cp}_2\text{Ti(IV)Cl}_2$  (Eq. (1)).  $\text{Cp}_2\text{Ti(III)Cl}$  (Eq. (1)) was reversibly combined with the polymeric growing chain  $\sim\text{PMMA}$  to form dormant species  $\sim\text{PMMA-Ti(IV)Cp}_2\text{Cl(C)}$  (Eq. (2)). The living characteristic of MMA radical polymerization was provided by the reversible end-capping of the propagating chain end by a second equivalent of  $\text{Cp}_2\text{Ti(III)Cl}$ . Then, the dormant species (Eq. (3)) obtained was activated by MAO to yield the Ti(IV) species which promoted the successive coordination polymerization of olefins (Eq. (4)). By terminated, 4-arms hydroxy-functionalized PMMA-*b*-PE MMA copolymer was formed (Eq. (5)).

To obtain the goal block copolymer, hydroxy-functionalized PMMA-*b*-PE copolymer, from the crude product, selective solvent extraction was carried out successively with boiling THF and  $\text{CHCl}_3$  solvents. It was found that THF was a good solvent for atactic PMMA, but was poor solvent for homopolyethylene. The amount of THF-soluble fraction was negligible ( $\leq 1\%$ ), but the amount of THF-insoluble fraction was over 99%, indicating that MMA-*E* block copolymer was obtained [12].  $\text{CHCl}_3$  was poor solvent for PE [13]. The amount of  $\text{CHCl}_3$ -insoluble fraction was trace which indicated that the metallocene  $\text{Cp}_2\text{TiCl}_2$  was completely consumed by the room temperature Zn reduction before the living radical polymerization of MMA. The generation of stable dormant species  $\sim\text{PMMA-Ti(IV)Cp}_2\text{Cl}$  was confirmed during the living radical

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