

# Synthesis of Well-Defined Star-Shaped Organosiloxane-Functionalized Polymethylmethacrylate Promoted by Epoxide-Derived Titanocene Alkoxides via Radical Polymerization

Lifu Ma, Weijiao Liu, Yaping Sheng, Qigu Huang, Wantai Yang

State Key Laboratory of Chemical Resource Engineering, Key Laboratory of carbon fiber and functional polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, China

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**ABSTRACT:** The star-shaped polymethylmethacrylate (PMMA) was synthesized via radical polymerization promoted by metallocene complexes in the presence of initiator of *tetra*(2,3-epoxy propoxy)silane ( $I_s$ ) and reducing agent Zn. The effect of temperature, time, molar ratio of monomer to initiator, and the structure of metallocene complexes on the polymerization performance was investigated. The structure and properties of the obtained polymer were characterized by gel permeation chromatography,

multiangle laser light scattering,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and WAXD. The results indicated that the obtained polymer was atactic-specific and featured narrow molecular weight distribution (1.30–1.57). Star-shaped organosiloxane-functionalized PMMA was produced. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1652–1658, 2011

**Key words:** metallocene catalysts; radical polymerization; star polymer; polyolefins

## INTRODUCTION

As a very promising aspect, polymerization of polar monomers such as methyl methacrylate (MMA),<sup>1</sup> chloromethyl styrene,<sup>2</sup> and acrylonitrile,<sup>3</sup> which can obtain corresponding popular polymer with high-molecular weight and monodispersity, has attracted much attention in both the scientific field and industry. In the beginning of the 1990s, Collins<sup>1</sup> and co-workers reported a two-component system consisting of neutral zirconocene ester enolate complex  $\text{Cp}_2\text{ZrMe}[\text{OC}(\text{Ot-Bu})\text{CMe}_2]$  as initiator and cationic zirconocene complex  $[\text{Cp}_2\text{ZrMe}(\text{THF})]^+[\text{BPh}_4]^-$  as catalyst polymerizing MMA in a living fashion to form syndiotactic-rich poly(methyl methacrylate) (PMMA) with high-molecular weight. Yasuda<sup>4</sup>

reported the synthesis of high-molecular weight PMMA with unusually narrow polydispersity, by the unique catalytic function of  $(\text{C}_5\text{R}_5)\text{LnR}'$  organolanthanide(III) complexes. Chen<sup>5</sup> developed a highly active catalyst system based on the  $\text{C}_s$ -ligated *ansa*-zirconocene ester enolate complexes, leading to the polymerization of highly syndiotactic PMMA at ambient temperature (25°C). The metallocene complexes controlled the stereostructure of the polymer and produced PMMA with syndiotactic,<sup>6</sup> isotactic-*b*-syndiotactic stereo-diblock,<sup>7</sup> or stereo-multiblock microstructure<sup>8</sup> not only in solution but also on surfaces or inside nanogalleries.<sup>9</sup> The effects of Lewis acid<sup>10</sup> and structure of *ansa*-zirconocene ester enolates<sup>11</sup> on polymerization of MMA were also investigated. Recently, Bhattacharjee<sup>12</sup> used  $\text{Cp}_2\text{TiCl}_2$  to catalyze MMA polymerization with high-molecular weight in aqueous condition ( $M_w = 51,000$ – $73,000$ ). As for forgoing mentioned reports, we can find that the stereoregulation of polymer is controllable, and the activity of catalyst system is relative highly to metallocene mediated coordination polymerization.

The initiating methodology of radical polymerization by metallocene radical was developed as well. Asandei<sup>13</sup> exploited a new route to initiate the radical polymerization with Ti metallocene/Zn/epoxide. The Ti (IV) complexes were reduced by reducing agents (e.g., Zn, Sm, Mn, and Al) to form  $\text{Ti}^{\bullet}(\text{III})$  radical. 4,4'-Methylenebis (*N,N*-diglycidylaniline)

Correspondence to: Q. Huang (qgh96@yahoo.com.cn).

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and POSS et al. were used as initiators to produce star-shaped polystyrene. The effects of reducing agents, temperature, ratio of Ti/Zn, ratio of Ti/epoxide,<sup>14</sup> ligands structure,<sup>15–17</sup> solvent, and additives<sup>18</sup> on styrene polymerization were investigated. The graft copolymer (styrene/MMA) was also synthesized through “grafting from” strategy.<sup>19</sup> In our previous work,<sup>20,21</sup> the synthesis of comblike hydroxy-functionalized aPS and the block copolymer of aPS-*b*-PE promoted by metallocene/Sn(Zn)/epoxides were investigated.

In this work, metallocene complexes Cp<sub>2</sub>TiCl<sub>2</sub> and CpTiCl<sub>3</sub> were used as catalytic precursors, zinc as reducing agent, and *tetra*(2,3-epoxy propoxy)silane (I<sub>s</sub>) as initiator prepared in our laboratory to promote MMA polymerization. Star-shaped PMMA containing organosiloxane group was obtained. The effects of polymerization conditions such as temperature, time, and molar ratio of initiator to monomer on polymerization performance were investigated.

## EXPERIMENTAL

### Materials

All operations of air- and moisture-sensitive materials were performed using the rigorous repellency of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold line under a dry argon atmosphere. Tetrahydrofuran (THF) and 1,4-dioxane were purified by refluxing over metal sodium under nitrogen for 48 h and distilled before use. Dicyclopentadiene, CuBr<sub>2</sub> (99%), SiCl<sub>4</sub> (99%), glycidol (99%), 2,2'-bipyridyl (bpy, 99%), and *n*-butyllithium (2.5M solution in hexane) were purchased from Acros in Beijing; TiCl<sub>4</sub>, Zinc powder (99%), and triethylamine were purchased from Beijing Chemical Agency, China; reagent-grade methylmethacrylate (MMA) was purified by extracting with 5% sodium hydroxide aqueous solution overnight and distilled from copper and calcium hydride under vacuum. All other chemicals were reagent grade or the best commercially available grade.

### Characterization

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were determined with INOVA 500 MHz in CDCl<sub>3</sub> (*d*<sub>1</sub>) at 25°C. Chemical shifts were referenced using internal solvent resonance and reported related to tetramethylsilane. WAXD was recorded with a Rigaku D/max 3A instrument, using Ni films to sieve wave, using Cu K $\alpha$  radiation ( $\lambda = 1.5405 \times 10^{-10}$  m). WAXD intensities were recorded from 5° to 40° with a continuous scanning speed. Molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography

(GPC) using a dual detector system consisting of a Waters 2410 differential refractometer, 996 photodiode array detector and styragel (HT3-HT5-HT6E) column, and a multiangle laser light scattering (MALLS) device, which was calibrated with polystyrene standards; THF was used as eluant. All polymers dissolved in THF under stirring at room temperature. The solutions were filtered through a Millipore Teflon filter (0.20- $\mu$ m pore size) before measurements. Monomer conversion was defined as the percentage of the weight of the product (g) to methyl methacrylate (MMA) (g) charged initially.

### Synthesis of catalysts and I<sub>s</sub>

CpTiCl<sub>3</sub> and Cp<sub>2</sub>TiCl<sub>2</sub> were prepared according to the literature.<sup>22</sup> Theoretical amount of cyclopentadiene was added to *n*-butyllithium solution to form cyclopentadienyllithium salt (Cp<sup>-</sup>Li<sup>+</sup>). The mixture reacted with TiCl<sub>4</sub> in tetrahydrofuran. The solvent was removed and the metallocene complex was recrystallized from methyl dichloride.

ANAL. Calcd for CpTiCl<sub>3</sub> (219, yield = 70.2%): C, 27.3; H, 2.28; Ti, 21.8; Cl, 48.5. Found: C, 27.3; H, 2.33; Ti, 22.1; Cl, 48.2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm): 6.50 (s, 5H, C<sub>5</sub>H<sub>5</sub>).

ANAL. Calcd for Cp<sub>2</sub>TiCl<sub>2</sub> (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. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm), 6.46 (s, 10H, C<sub>10</sub>H<sub>10</sub>).

*Tetra*(2,3-epoxy propoxy)silane (I<sub>s</sub>): In 300-mL flamed Schlenk flask under nitrogen atmosphere, 150 mL THF as solvent, 5.0 mL SiCl<sub>4</sub> (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°C for 10 h. The mixture was filtrated at rt. The solvent was removed by vacuum. *Tetra*(2,3-epoxy propoxy)silane (I<sub>s</sub>) was obtained colorless liquid, yield: 65.2%.

ANAL. Calcd for Si(C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>)<sub>4</sub>(FM: 320, bp: 346.1°C): C, 45.0; H, 6.25. Found: C, 45.8; H, 6.30. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>,  $\delta$ , ppm), 2.67–2.80 (m, 2H), 3.14(m, 1H), 3.50–3.82(m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), three signals at  $\delta$  37.1, 43.6, and 63.3 ppm were observed.

### Synthesis of star-shaped polymer

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 precursors (Cp<sub>2</sub>TiCl<sub>2</sub> or CpTiCl<sub>3</sub>), reducing agent (Zn) in desired molar ratio, and 10-mL freshly distilled 1,4-dioxane were added into a 200-mL Schlenk flask, 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 flask was then cooled to  $-78^{\circ}\text{C}$  by liquid nitrogen. A mixture of monomer (MMA), initiator ( $I_s$ ),  $\text{CuBr}_2$ , and bpy in desired molar ratio was added under argon. The reactor was degassed and placed into an oil bath at predetermined temperature. 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. The reaction lasted to desired time and was terminated by excess amount of methanol/HCl (100/10, v/v) solution. The obtained PMMA was filtered and dried. Asandei<sup>13,19</sup> reported the mechanism of the living radical polymerization of styrene and MMA. Here, we simply described the synthesis course of the  $\text{Cp}_2\text{TiCl}$ -catalyzed MMA polymerization initiated by a novel initiator, epoxide ( $I_s$ ) (Scheme 1), where  $I_s$  corresponded to *tetra*(2,3-epoxypropoxy)silane.

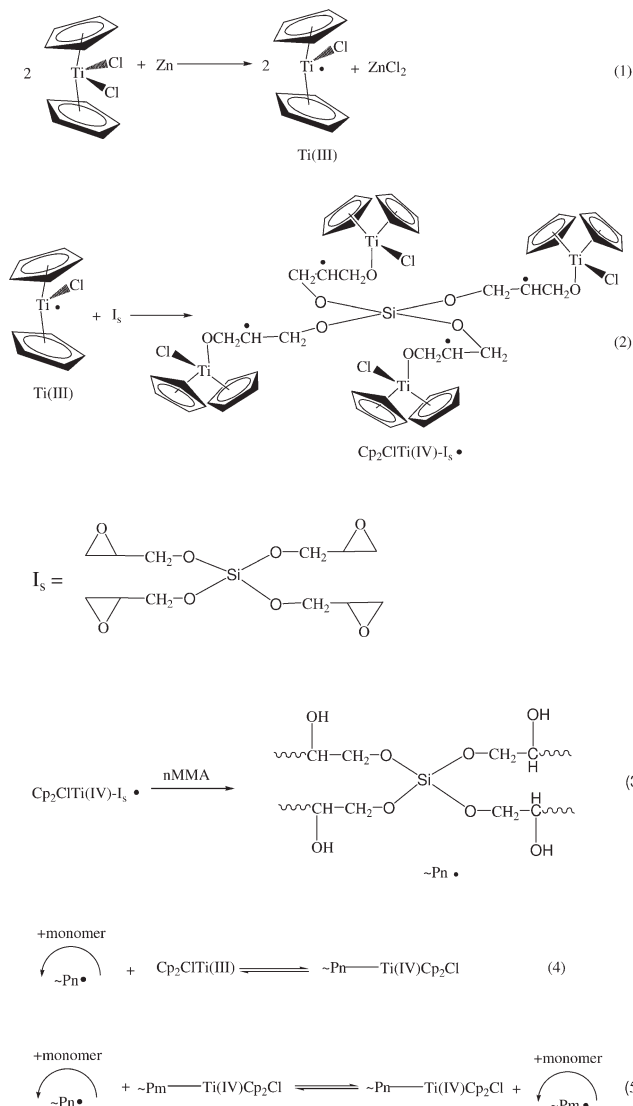
## RESULTS AND DISCUSSION

### Synthesis of star-shaped polymer

In a typical reaction, the well-defined star-shaped PMMA samples with various molecular weights were synthesized via radical polymerization using  $\text{Cp}_2\text{TiCl}_2/\text{Zn}/I_s$  as catalyst system. The  $\text{CuBr}_2$  and bpy were used to keep the polymerization in living manner. The roles of  $\text{CuBr}_2$  and bpy for the polymerization were described in the literature.<sup>19</sup> Following this *in situ* generation of  $\text{Cp}_2\text{Ti}^{\bullet}\text{Cl}$  [eq (1) in Scheme 1], the initiation radical was formed after the injection of the mixture of  $I_s$ , MMA,  $\text{CuBr}_2$ , and bpy [eqs. (2) and (3) in Scheme 1]. The mixture color was rapidly changed, indicating the consumption of  $\text{Cp}_2\text{Ti}^{\bullet}\text{Cl}$  by epoxide RRO. The RRO proceeded with the formation of Ti alkoxides radical ( $\text{Cp}_2\text{TiCl-O-}I_s$ ).

The effect of conditions such as temperature and time on the polymerization of MMA was summarized in Table I.

From Table I (runs 1–3), one can notice that the  $M_n$  of the PMMA obtained and the monomer conversion increased with the increasing of the temperature from 50 to  $90^{\circ}\text{C}$ , and the MWD of the polymers was at the narrow range from 1.38 to 1.46, which indicated that the catalytic active center was stable, and the chain propagation rate was enhanced during the temperature scale. However, the molecular weight of the polymers and the monomer conversion decreased when the temperature was over  $90^{\circ}\text{C}$  (run 4 in Table I), resulting from the faster deactivation rate of the active species at higher temperature.  $M_n$  determined by MALLS was linear with polymerization time (runs 5, 6, 7, 3, and 8 in Table I), implying that the polymerization behavior was in living



**Scheme 1** MMA polymerization course and the structure of initiator  $I_s$ .

manner. However, the calculated values of  $M_n$  were all less than the  $M_n$  values found by MALLS. As shown in Tables I and II, the data of the obtained polymers  $M_n$  determined by GPC and MALLS were considerable different. The possible reasons are similar to the literature.<sup>21</sup>

The MWD of the polymers increased slightly over  $90^{\circ}\text{C}$ , which was related to the increase of side reactions and the shift of the reversible dissociation equilibrium toward the active species. The monomer conversion and  $M_n$  of the obtained polymers became higher, but the MWD of the polymer came slightly down when the polymerization time lasted from 4 to 10 h (runs 5–7, 3 in Table I). In addition, the initiating efficiency (I.E.) was sensitive to temperature. I.E. was enhanced from 0.45 to 0.73 when the temperature increased from 50 to  $90^{\circ}\text{C}$  (runs 1–3 in Table I). The I.E., however, was not obviously

**TABLE I**  
Effect of Conditions on Polymerization of MMA Catalyzed by  $\text{Cp}_2\text{TiCl}_2/\text{Zn}/\text{I}_s$  Catalyst System

Run	$T_p$ (°C)	Time (h)	$M_n^a \times 10^{-4}$	$M_n^b \times 10^{-4}$	$M_n^c \times 10^{-4}$	$M_w/M_n^c$	Cond <sup>d</sup> (wt %)	IE <sup>e</sup>
1	50	10	1.12	1.32	2.93	1.30	33	0.45
2	70	10	2.52	3.62	6.46	1.31	63	0.56
3	90	10	2.72	4.90	6.71	1.29	86	0.73
4	110	10	2.68	3.81	5.08	1.77	73	0.75
5	90	4	0.44	0.50	0.67	1.34	33	0.74
6	90	6	1.21	2.04	2.72	1.32	52	0.75
7	90	8	2.01	3.49	4.65	1.31	69	0.75
8	90	12	2.91	6.39	8.63	1.26	92	0.74

Reaction conditions: MMA/ $\text{I}_s$ / $\text{Cp}_2\text{TiCl}_2/\text{Zn}$  = 200/1/8/5;  $\text{Cp}_2\text{TiCl}_2/\text{CuBr}_2/\text{bipyridyl}$  = 1 : 1 : 2.5; monomer: MMA (4 mL); solvent: 1,4-dioxane (10 mL).

<sup>a</sup> Determined by GPC.

<sup>b</sup> Calculated molecular weight.

<sup>c</sup> Determined by MALLS.

<sup>d</sup> Monomer conversion.

<sup>e</sup> The initiation efficiency determined by calculated  $M_n^b/M_n^c$  by MALLS.

changed during the experimental time scale from 4 to 12 h, basically kept at the range of 0.74–0.75. These results implied that the amount of the chain growing active species was depended on the temperature, but it could keep constant when the temperature was maintained during the polymerization course. At higher temperature, for example, at 110°C, however, the molecular weight of the polymer was decreased, which implied that the active species was becoming deactivated. The MWD of the polymer obtained under this condition became broad, which might result from an increasing incidence of side reactions. But the MWD value of 1.77 of this polymer (run 4 in Table I) was narrower than that of aPS initiated by the similar catalyst system at 110°C,<sup>21</sup> implying that this catalyst system is better for MMA polymerization in a pseudoliving manner even at wider temperature scale.

The effect of the  $[\text{MMA}]/[\text{I}_s]$  molar ratio on the polymerization behavior was evaluated while maintaining a constant  $\text{Cp}_2\text{TiCl}_2/\text{Zn}/\text{I}_s$  = 8/5/1 ratio. The result was compiled in Table II and Figure 1.

From Table II, it can be found that the monomer conversion was increased with the increasing of polymerization time. From 4 to 10 h, the  $M_n$  value of the PMMA obtained under the condition of  $[\text{MMA}]/[\text{I}_s]$  = 100, 200, and 400 increased from  $0.59 \times 10^4$  g/mol to  $6.11 \times 10^4$  g/mol (runs 9–12),  $0.67$ – $6.71 \times 10^4$  g/mol (runs 5–7 and 3), and  $0.51$ – $4.15 \times 10^4$  g/mol (runs 13–16), respectively. However, the MWD of the polymers came down from 1.35 to 1.33 (runs 9–12), 1.34 to 1.29 (runs 5–7 and 3), and 1.41 to 1.33 (runs 13–16). The monomer conversion was high, 70 and 86%, respectively, when the  $[\text{MMA}]/[\text{I}_s]$  molar ratio was 100 and 200 after 10 h (runs 12 and 3 in Table II). But it decreased to 58.2% when the

**TABLE II**  
Effect of MMA/ $\text{I}_s$  Ratio on the Polymerization

Run	$[\text{MMA}]/[\text{I}_s]$ (mol/mol)	Time (h)	Conversion (wt %)	$M_n \times 10^{-4a}$ (g/mol)	$M_w/M_n^a$	$M_n^b \times 10^{-4}$	IE <sup>c</sup>
9	100	4	27	0.59	1.35	0.42	0.71
10	100	6	41	2.51	1.35	1.78	0.71
11	100	8	55	4.33	1.33	3.07	0.71
12	100	10	70	6.11	1.33	4.21	0.69
5	200	4	33	0.67	1.34	0.49	0.74
6	200	6	52	2.72	1.32	2.04	0.75
7	200	8	69	4.65	1.31	3.44	0.74
3	200	10	86	6.71	1.29	4.90	0.73
13	400	4	22.7	0.51	1.41	0.31	0.62
14	400	6	33.9	1.73	1.35	1.07	0.62
15	400	8	46.1	2.95	1.34	1.77	0.60
16	400	10	58.2	4.15	1.33	2.57	0.62

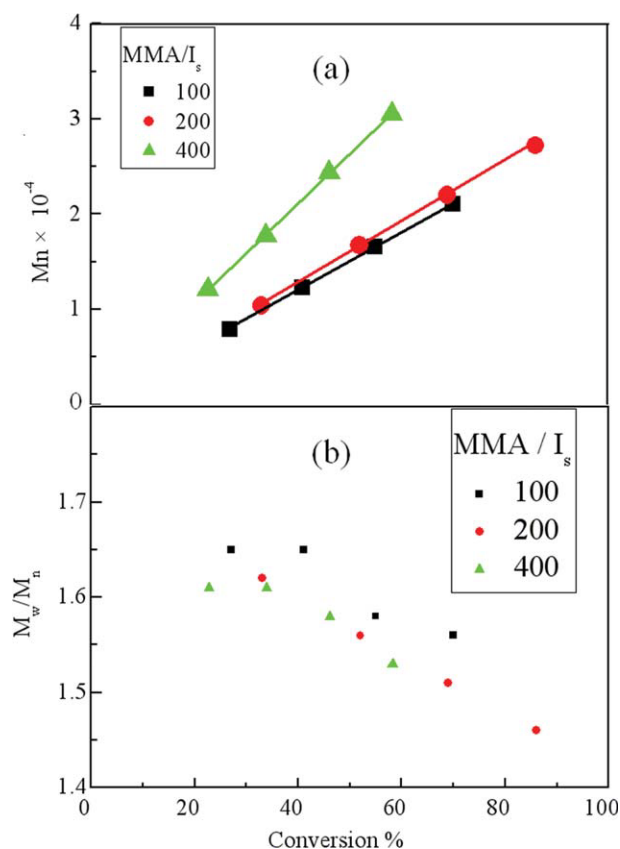
Polymerization conditions: polymerization temperature, 90°C; solvent, 1,4-dioxane, 10 mL; MMA: 2 mL ( $[\text{MMA}]/[\text{I}_s]$  = 100), 4 mL ( $[\text{MMA}]/[\text{I}_s]$  = 200), 8 mL ( $[\text{MMA}]/[\text{I}_s]$  = 400);  $\text{Cp}_2\text{TiCl}_2/\text{Zn}/\text{I}_s$  = 8/5/1;  $\text{Cp}_2\text{TiCl}_2/\text{CuBr}_2/\text{bpy}$  = 1 : 1 : 2.5.

<sup>a</sup> Determined by MALLS.

<sup>b</sup> Calculated molecular weight.

<sup>c</sup> The initiation efficiency determined by calculated  $M_n^b/M_n^a$  by MALLS.





**Figure 1** Effect of  $\text{MMA}/I_s$  molar ratio on the polymerization. [Color figure can be viewed in the online issue, which is available at [www.wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]

$[\text{MMA}]/[I_s]$  ratio was 400 (run 16 in Table II). These results indicated that relative high-monomer conversion (86%) and narrower MWD of the star-shaped polymer obtained were performed under the typical condition of  $[\text{MMA}]/[I_s] = 200$  (run 3 in Table II).

The I.E. was about 0.71 and 0.74 when  $[\text{MMA}]/[I_s] = 100$  and 200, respectively. But it decreased to about 0.62 when  $[\text{MMA}]/[I_s] = 400$ . It was possible that the metallocene radical and  $I_s$  concentration decreased with increasing of the amount of MMA in the mixture and the reaction rate of the metallocene radical with  $I_s$  decreased, so that the amount of the chain growing radical Ti alkoxides radical ( $\text{Cp}_2\text{TiCl-O-I}_s$ ) was less.

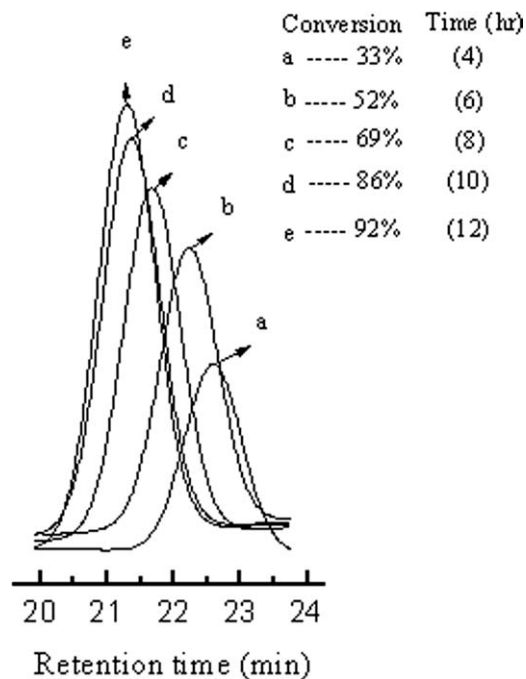
The pseudolinear dependence of the  $M_n$  on monomer conversion [Fig. 1(a)] was observed in all cases, indicating that the radical concentration changed slightly during the polymerization process. A relative narrow MWD occurred for  $[\text{MMA}]/[I_s] = 100$ , 200, and 400 [Fig. 1(b)]. The MWD values of the obtained polymers were not sensible to the molar ratio of  $[\text{MMA}]/[I_s]$  and were within a narrow range of 1.31–1.61. So the Ti-mediated MMA polymerizations initiated from  $I_s$  could be attributed to the

pseudoliving behavior, but not rigorously to definition of the "living polymerization."<sup>23</sup>

Reaction conditions:  $\text{Cp}_2\text{TiCl}_2/\text{Zn}/I_s = 8/5/1$ ; monomer: MMA (4 mL); solvent: 1,4-dioxane (10 mL); temperature: 90°C.

The synthesis of the star-shaped polymer at the ratio of  $\text{Cp}_2\text{TiCl}_2/\text{Zn}/I_s/\text{MMA} = 8/5/1/200$  was investigated, and the GPC results of these samples were showed in Figure 2.

From Figure 2, one can notice that the GPC curves shifted to lower retention time when the monomer conversion was increased. Under the conditions of monomer conversion of 86% and the reaction time of 10 h (curve d in Fig. 2), the number-average molecular weight was up to  $2.72 \times 10^4$  g/mol (run 3 in Table I). However, the  $M_n$  of the polymer was just  $0.44 \times 10^4$  g/mol (run 5 in Table I, curve a in Fig. 2) when the reaction time lasted to 4 h and the monomer conversion was 33%. It indicated that the  $M_n$  of the obtained polymer increased with increasing of the monomer conversion and polymerization time. However, when the time was lasted to 12 h, although the monomer conversion was up to 92%, the  $M_n$  of the polymer up to  $2.91 \times 10^4$  g/mol was observably less than that expected ( $3.48 \times 10^4$  g/mol) (curve e in Fig. 2). This appearance might result from fairly low-monomer concentration in the poststage of the polymerization.



**Figure 2** GPC curves of the obtained polymer with different monomer conversion. Reaction conditions:  $\text{Cp}_2\text{TiCl}_2/\text{Zn}/I_s/\text{MMA} = 8/5/1/200$ ;  $\text{Cp}_2\text{TiCl}_2/\text{CuBr}_2/\text{bpy} = 1 : 1 : 2.5$ ; monomer: MMA (4 mL); solvent: 1,4-dioxane (10 mL); temperature: 90°C.

**TABLE III**  
The Effect of Metallocene Complexes and Reducing Agents on the Polymerization of MMA

Run	Catalyst	Reducing agent	$M_n \times 10^{-4a}$ (g/mol)	$M_w/M_n^a$	$M_n^b \times 10^{-4}$	Conversion (wt %)	IE
3	Cp <sub>2</sub> TiCl <sub>2</sub>	Zn	6.71	1.29	4.90	86	0.73
17	CpTiCl <sub>3</sub>	Zn	6.99	1.43	3.00	62	0.43
18	Cp <sub>2</sub> TiCl <sub>2</sub>	–	41.5	2.40	0.83	39	0.02
19	CpTiCl <sub>3</sub>	–	38.1	2.52	0.76	38	0.02

Reaction conditions: catalysts/reducing agents/I<sub>s</sub>/MMA = 8/5/1/200; catalysts/CuBr<sub>2</sub>/bpy = 1 : 1 : 2.5; monomer: MMA (4 mL); solvent: 1,4-dioxane (10 mL); temperature: 90°C; time, 10 h.

<sup>a</sup> Determined by MALLS.

<sup>b</sup> Calculated molecular weight.

<sup>c</sup> The initiation efficiency determined by calculated  $M_n^b/M_n^a$  by MALLS.

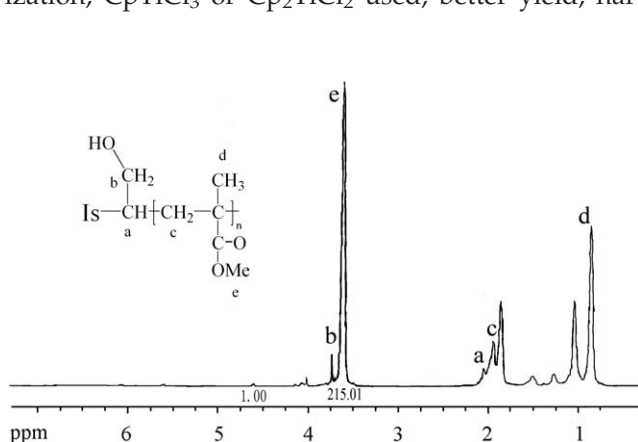
### Metallocene complexes

The effect of metallocene complexes on the MMA polymerization performance was compiled in Table III.

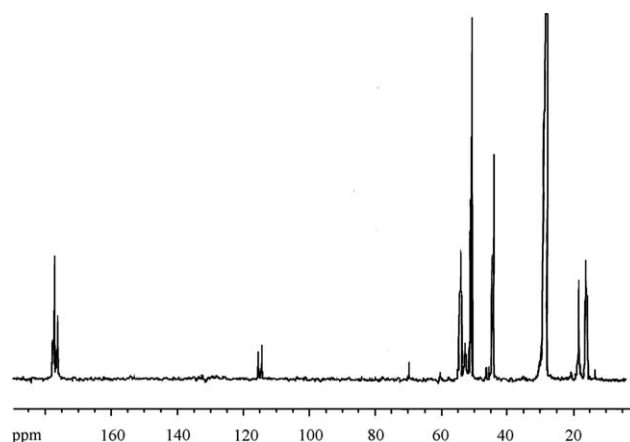
We evaluated the influence of metallocene complexes using Zn as reducing agent (run 3 and 17 in Table III). The results showed that Cp<sub>2</sub>TiCl<sub>2</sub> using as catalyst for MMA polymerization led to higher monomer conversion,  $M_n$  and I.E. (86%, 6.71 × 10<sup>4</sup> g/mol and 0.73, respectively), and narrower MWD (1.29). By contrast, the yield and I.E. for the polymerization of MMA initiated by CpTiCl<sub>3</sub> were obviously lower (62% and 0.43, respectively), and the value of  $M_n$  and MWD became higher (6.99 × 10<sup>4</sup> g/mol and 1.43, respectively), indicating that the CpTiCl<sub>3</sub> was not as efficient as sandwich metallocene Cp<sub>2</sub>TiCl<sub>2</sub> for MMA polymerization. The reduced I.E. and broader MWD for CpTiCl<sub>3</sub> can be explained by the electron donating effect of ligand. The two Cp rings in Cp<sub>2</sub>TiCl<sub>2</sub> further decreases the Lewis acidity at the Ti center, and while their combined electron donating effect strengthens the C-Ti chain end bond versus CpTiCl<sub>3</sub>.<sup>24</sup> The experiments demonstrated that in the presence of Zn as reducing agent for MMA polymerization, CpTiCl<sub>3</sub> or Cp<sub>2</sub>TiCl<sub>2</sub> used, better yield, nar-

rower MWD, and higher I.E. (runs 3 and 17 in Table III) than the simply uncontrolled thermally initiated polymerization (runs 18 and 19 in Table III) under the absence of Zn at 90°C. These results confirmed that the thermal polymerization of MMA was neglectable in the absence of Zn and the radical was produced in the presence of Zn.<sup>25</sup>

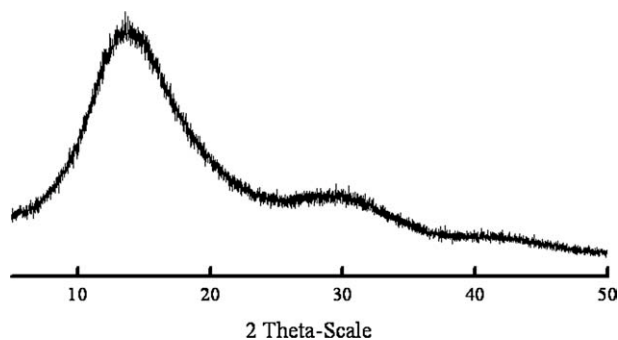
For the <sup>1</sup>H NMR spectrum of the star-shaped PMMA (Fig. 3), a signal assigned to methoxy protons appeared at δ 3.6 ppm. Methyl protons appeared at the region between δ 0.9 and 1.02 ppm and methylene protons at the region between δ 1.75 and 2.01 ppm. The methylene protons would appear at δ 1.83 ppm attributed to the characteristic signal of syndiotactic PMMA. A double signal at δ 1.62 and 2.33 ppm would be observed for isotactic PMMA.<sup>26,27</sup> In this case, neither of these characteristic peaks was observed; therefore, it could conclude that an atactic PMMA was formed. Three signals at δ 2.6–2.7, 3.12–3.18, and 3.75–3.85 ppm by <sup>1</sup>H NMR spectrum and three signals at δ 37.5, 46.2, and 61.5 ppm by <sup>13</sup>C NMR spectrum (Fig. 4) attributed to I<sub>s</sub> residue were observed. The results indicated that the



**Figure 3** The <sup>1</sup>H NMR spectrum from the star-shaped PMMA sample (run 3 in Table I). Reaction conditions: Cp<sub>2</sub>TiCl<sub>2</sub>/Zn/I<sub>s</sub>/MMA = 8/5/1/200; Cp<sub>2</sub>TiCl<sub>2</sub>/CuBr<sub>2</sub>/bpy = 1 : 1 : 2.5; monomer: MMA (4 mL); solvent: 1,4-dioxane (10 mL); temperature: 90°C; time: 10 h.



**Figure 4** The <sup>13</sup>C NMR spectrum of the star-shaped PMMA sample (run 3 in Table I). Reaction conditions: Cp<sub>2</sub>TiCl<sub>2</sub>/Zn/I<sub>s</sub>/MMA = 8/5/1/200; monomer: MMA (4 mL); solvent: 1,4-dioxane (10 mL); temperature: 90°C; time: 10 h.



**Figure 5** The WAXD spectrum of the star-shaped PMMA (sample 3 in Table I).

obtained PMMA was initiated by *tetra*(2,3-epoxy propoxy)silane.

FTIR result also confirmed that the opening of the epoxide ring of  $I_s$  promoted by metallocene complex radical  $CpTi^{\bullet}(III)Cl_2$  took place by entire disappearing of the signal at  $910.4\text{ cm}^{-1}$  attributed to epoxy group. It implied that all epoxy groups (4) of  $I_s$  were opened by metallocene complex radical to form chain growing radical which initiated MMA polymerization in living characteristics. Asandei<sup>13</sup> reported all epoxy groups of the initiators, such as 4,4'-methylenebis (*N,N*-diglycidylaniline) and POSS et al., and opened by the metallocene radical to initiate styrene polymerization in living characteristics simultaneously.

### <sup>13</sup>C NMR and WAXD analysis

The <sup>13</sup>C NMR spectrum from the sample (run 3 in Table I) catalyzed by  $Cp_2TiCl_2/Zn/I_s$  was shown in Figure 4. Multiplets were observed at  $\delta$  176–178 ppm assigned to the ester carbon, confirming the atactic nature of the obtained polymer.<sup>28</sup> The peaks at  $\delta$  44 and  $\delta$  16–18 ppm were attributed to methylene and methyl carbons. The methoxy carbon appeared at  $\delta$  51 ppm. The WAXD of the same sample (run 3 in Table I) showed just a wide peak at  $2\theta = 10^\circ\text{--}20^\circ$  and a wide and weak peak at  $2\theta = 25^\circ\text{--}33^\circ$ , which implied the obtained polymer featured atactic nature (Fig. 5).

Reaction conditions:  $Cp_2TiCl_2/Zn/I_s/MMA = 8/5/1/200$ ; monomer: MMA (4 mL); solvent: 1,4-dioxane (10 mL); temperature:  $90^\circ\text{C}$ ; time: 10 h.

### CONCLUSIONS

Well-defined star-shaped atactic PMMA with functional group (hydroxyl) promoted by metallocene complexes/reducing agents/ $I_s$  was synthesized. The effect of temperature, time, MMA/ $I_s$  ratio, and metallocene complexes on MMA polymerization was investigated. The polymer yield initiated by  $Cp_2TiCl_2/Zn/$

$I_s$  system was higher (86%), and the obtained polymer owned high  $M_n$  ( $2.72 \times 10^4\text{ g/mol}$ ) and narrower MWD. The linear dependence of  $M_n$  on monomer conversion in all cases within the range of  $[MMA]/[I_s] = 100\text{--}400$  were not rigorous, and the subsequent evaluation of corresponding kinetics of the Ti-mediated MMA polymerizations initiated by  $I_s$  indicated that the polymerization process could be attributed to the pseudoliving behavior. Star-shaped organosiloxane-functionalized PMMA was produced. The result of <sup>13</sup>C NMR indicated that the obtained polymer was atactic-specific.

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