

Synthesis of Polyolefin/Poly(methyl methacrylate) Block Copolymer Using Zirconocene Catalyst System

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ABSTRACT: The reactions of methyl methacrylate (MMA) or I₂ with the living zirconium-polyolefin bond (Zr-PO) using zirconocene catalyst system were examined. Although the reaction of MMA with the living Zr-PP does not proceed, I₂ readily reacts with the living Zr-PO, such as atactic polypropylene (ataPP), iso poly(1-hexene) and syndiotactic poly(propylene) (synPP), quantitatively to give the terminal iodized polyolefins (PO-I). Moreover, PO-poly(methyl methacrylate) (PMMA) block copolymers could be obtained by the reaction of MMA with living Sm-PO, which was formerly prepared by the transformation of PO-I by Cp^{*}Sm.

KEY WORDS Poly(olefin)-*block*-Poly(methyl methacrylate) / Zirconocene Catalyst / Living Polymerization / Iodine / Samalocene /

Block copolymerizations of olefins with polar monomers remain an ultimate goal in the polyolefin chemistry. For that purpose, the reaction between living polyolefin and (meth)acrylate, such as MMA, has been investigated.

A block copolymerization of propylene with MMA by a V(acac)₃/AlEt₂Cl system^{1,2} and a block copolymerization of olefins (C₂,5,6) with (meth)acrylate, such as MMA, methyl acrylate (MA) and ethyl acrylate (EA), using lanthanocene complex^{3,4} may be the sole examples of this type of the reaction.

On lanthanide system, it has been also demonstrated the transformation of cationic growing center of poly(tetrahydrofuran) (PTHF) into anionic species directly by SmI₂ using poly(*t*BuMA)^{5a,b)} or indirectly by KI/Cp^{*}Sm using poly(alkyl methacrylate), such as MMA, ethyl methacrylate (EtMA), *i*PrMA, *n*BuMA.^{5c)}

Concerning group IV metallocene catalysts, Collins *et al.* described the living polymerization of MMA catalyzed by the two component system consisting of the cationic zirconocene complex and the neutral enolate complex.^{6a)–c)} Shiono *et al.* reported that the cationic zirconocene complexes formed from dimethylzirconocenes and B(C₆F₅)₃ or B(C₆F₅)₄[–] polymerize MMA in the well controlled manner when activated with the third component, such as alkyl zinc or alkyl aluminum compounds.^{7a)–e)}

Recently, Collins *et al.* published the first polymerization of MMA with a single component cationic zirconocene enolate complex.^{6d)} Gibson *et al.* have studied MMA polymerization with cationic zirconocene complexes formed from dimethylzirconocenes and

B(C₆F₅)₃.⁸ Höcker *et al.* showed that the cationic zirconocene complexes, for example, (Me₂C) Cp₂ZrMe(thf)⁺BPh₄[–] or (Me₂C) CpIndZrMe(thf)⁺BPh₄[–] are active for living polymerization of MMA.^{9a),b)}

In previous communication,^{10a),b)} we showed that simple Cp₂ZrMe₂/B(C₆F₅)₃ system with or without AlOct₃ as a scavenger promotes the living polymerization of propylene at –78°C, and that *rac*-(Et)Ind₂ZrMe₂/B(C₆F₅)₃ system also promotes the isospecific living polymerization of 1-hexene at –78°C. More recently, we also demonstrated that the syndiospecific living like polymerization of propylene takes place with mixed metallocene system, for example using (Ph₂C)CpFluZrCl₂/B(C₆F₅)₃/Cp^{*}TiMe₃ at –50°C.^{11a)}

In this work, the reactions of MMA or I₂ with the living Zr-PO is investigated in order to make clear the reactivity of the “living” active sites of Zr-PO bonds to metallocene active species. PO-PMMA block copolymers with different type of stereospecificity in PO segment was synthesized, directly or indirectly.

EXPERIMENTAL

Materials

Cp₂ZrMe₂, Cp₂HfMe₂, *rac*-(Et)Ind₂ZrMe₂, and (Ph₂C) CpFluZrCl₂ were synthesized according to the procedure reported in the literature.¹² Cp^{*}TiMe₃ was purchased from Strem Chemicals Inc., tris(pentafluorophenyl) borane and trioctylaluminum were purchased from Tosoh-Akzo Chemical Co. and they were used without further purification. Propylene (from Takachiho Chemical Industrial Co. Ltd.) was purified through NaOH and P₂O₅. Toluene, 1-hexene, MMA

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Table I. Results of the MMA reaction with living PP or poly(1-hexene) end prepared with Cp₂ZrMe₂/B(C₆F₅)₃ or Cp₂HfMe₂/B(C₆F₅)₃ catalyst

Run	Temp/°C	Time/h	Yield/mg	M _n	M _w /M _n
1	-78 to 0	10	89.1	5200	1.08
2	-50	92	755	1130000/6200	1.89/1.05

Polymerization conditions: Run 1: toluene = 13 mL, B = 400 μmol, Zr = 40 μmol, propylene = 83 mmol, temp = -78°C, time = 12 h. Run 2: toluene = 9.5 mL, B = 400 μmol, Hf = 40 μmol, 1-hexene = 83 mmol, temp = -50°C, time = 29 h. Reaction conditions: Run 1: MMA = 8 mmol. Run2: MMA = 80 mmol. M_n: Determined by GPC (THF at 40°C) using PS standards.

was purified according to the usual procedure. Iodine was used without further purification.

Reaction of the Living PO with MMA

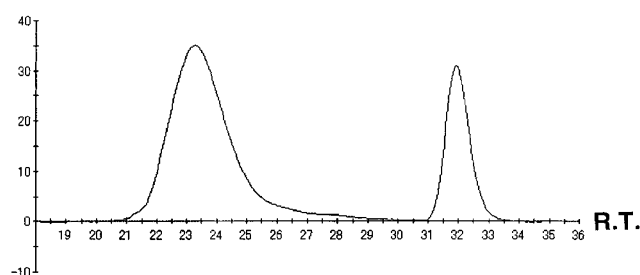
Polymerization of propylene was carried out in a 100 mL stainless steel autoclave by batchwise operation in toluene (total volume = 13 mL). Borane (360 μmol) as a scavenger was added, and the reactor was cooled in a methanol bath cooled to -78°C. After the addition of Cp₂ZrMe₂ and B(C₆F₅)₃ (Zr = B = 40 μmol) to the reactor, the polymerization was started by introduction of liquid propylene (83 mmol). And the polymerization was conducted for 12 h, MMA (8 mmol) was added and the mixture was hold for 10 h by raising temperature from -78°C to 0°C. The mixture was quenched by addition of HCl/methanol solution. The polymer was washed with excess methanol and dried under vacuum at room temperature.

Polymerization of 1-hexene with Cp₂HfMe₂ at -50°C and reaction of living poly(1-hexene) with MMA (80 mmol) was also conducted according to the same procedure as the case of propylene.

Reaction of the Living PO with I₂¹³

Polymerization of propylene was conducted in an autoclave in toluene (total volume = 14.4 mL). Tri-octylaluminium (800 μmol) as a scavenger was added, and the reactor was cooled in a methanol bath kept at -78 or -50°C. After the addition of zirconocene and B(C₆F₅)₃ (Zr = B = 40 μmol) to the reactor (in the case with Cs symmetric zirconocene, 40 μmol of Cp*TiMe₃ was added), the polymerization was started by introduction of liquid propylene (83 mmol). After the polymerization was conducted for a given time, I₂ (3 mmol)/toluene (6 mL) mixture was added to the reactor, followed by standing for 15 h. The mixture was quenched by using methanol. The polymer produced was washed with excess methanol and dried under vacuum at room temperature.

Polymerization of 1-hexene with C₂ symmetric zirconocene and reaction of living iso poly(1-hexene) with I₂ were also conducted according to the same procedure as the case of propylene.

**Figure 1.** GPC curves for PP/PMMA (run2).

Reaction of the PO-I with Cp*₂Sm and Block Copolymerization with MMA

The solution of ataPP-I (4.2 μmol) in toluene was cooled at 0°C. After the addition of the Cp*₂Sm (9 μmol)/toluene solution, the mixture (total toluene volume 0.85 mL) was stirred for 3 min. The copolymerization was started by introduction of MMA (0.9 mmol) at 0°C, followed by standing for 1 h. The mixture was quenched by addition of methanol.

Reaction of the iso poly(1-hexene)-I with Cp*₂Sm and MMA were also conducted according to the same procedure as the case of ataPP-I.

Analytical Procedure

Molecular weights and molecular weight distributions of polymer were determined by GPC (TOSOH 8020 series) at 40°C using THF as eluent or HTGPC (TOSOH HLC-8121GPC/HT) at 135°C using 1, 2, 4-trichlorobenzene as eluent. ¹H and ¹³C NMR spectra were recorded on a JEOL GSX series spectrometer operated at 270 and 68 MHz, respectively, in pulse Fourier transform mode. CDCl₃ and tetrachloroethane-*d*₂ solvent were used for the NMR measurement.

RESULTS AND DISCUSSION

Reaction of the Living PO with MMA

Table I shows the results of the reaction of MMA with the living PP or poly(1-hexene) prepared with Cp₂ZrMe₂/B(C₆F₅)₃ or Cp₂HfMe₂/B(C₆F₅)₃ catalyst.

¹H NMR spectrum of run 1 is polypropylene homopolymer.¹⁴

Figure 1 shows the GPC result of run 2 which dis-

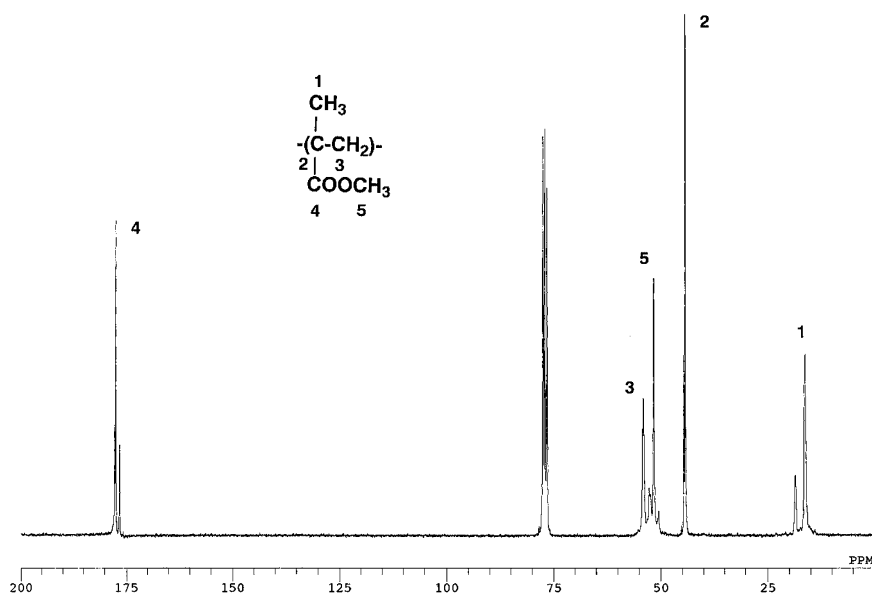


Figure 2. ^1H NMR spectrum of hexane insoluble part (run 2).

Table II. Results of the iodine reaction with living PO prepared with various metallocene catalyst systems

Run	Polymer	Yield/mg	M_n	M_w/M_n	M_n (^1H NMR)
3	ataPP	84.7	8400	1.19	8400
4	iso poly(1-hexene)	47.8	4900	1.21	4600
5	synPP	6.2	9700	1.37	10000

Polymerization conditions: Run 3: toluene = 14.4 mL, Al = 800 μmol , Zr = B = 40 μmol , propylene = 83 mmol, temp = -78°C , time = 4 h. Run 4: toluene = 11 mL, Al = 800 μmol , Zr = B = 40 μmol , 1-hexene = 83 mmol, temp = -78°C , time = 8 h. Run 5: toluene = 14.4 mL, Al = 800 μmol , Zr = B = Ti = 40 μmol , propylene = 83 mmol, temp = -50°C , time = 6 h. Reaction conditions: Run 3, 4: I_2 = 3 mmol, temp = -78°C , time = 17, 14 h. Run 5: I_2 = 3 mmol, temp = -50°C , time = 15 h. Yield: Run 5: hexane insoluble fraction. M_n : Run 3, 5: Determined by HTGPC (TCB at 140°C) using PP standards. Run 4: Determined by GPC (TCB at 40°C) using PS standards.

plays bimodal molecular weight distribution (MWD) as shown in Table I. The lower molecular weight polymer shows a narrow MWD at around 1.05–1.1 (see Table I).

^1H NMR spectra of run 2 with low molecular weight shows poly(1-hexene) homopolymer soluble in hexane and that insoluble in hexane with high molecular weight is PMMA (Figure 2).

The number of polymer chains (N) of PHx calculated from fractionated yield and M_n was 32 μmol , while that of N value of PMMA was 0.5 μmol .

The M_n of the PHx obtained at early stage of polymerization increased with increasing polymerization time ($M_n = 1700/6600$, MWD 1.13/1.05 at 5/29 h, respectively).¹⁵ However, the M_n at later stage did not increase ($M_n = 6200$, MWD = 1.05 at 92 h). Thus, the reaction of MMA with PO-Zr did not occur.

Reaction of the Living PO with I_2

Run 3–5 in Table II are the results of the reaction of I_2 at low temperature with living polyolefins prepared with various metallocene catalyst systems (run 3: ataPP with $\text{Cp}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3/\text{AlOct}_3$ at

-78°C , run 4: iso poly(1-hexene) [mmmm = 0.88] with *rac*-(Et) $\text{Ind}_2\text{ZrMe}_2/\text{B}(\text{C}_6\text{F}_5)_3/\text{AlOct}_3$ at -78°C , run 5: synPP [rrrr = 0.94] with $(\text{Ph}_2\text{C})\text{CpFluZrCl}_2/\text{B}(\text{C}_6\text{F}_5)_3/\text{Cp}^*\text{TiMe}_3/\text{AlOct}_3$ at -50°C ^{10,11a,b}). All polyolefins obtained showed narrow MWDs.

To check the incorporation of iodine into the polymer end, ^1H NMR spectrum was measured. The run 3 in Table II shows the resonance attributable to methylene protons adjacent to iodine at around 3.1 ppm (Figure 3), while the resonance attributable to a methine proton adjacent to iodine was not observed at around 4 ppm. Therefore, the polymerization of olefin is considered to proceed by the 1, 2-insertion.

The molecular weights were estimated from the relative intensity between the methylene chain end and the main chain (0.25–1.75 ppm). The calculated values were almost the same as M_n s obtained by GPC (see Table II), which indicates that every living polyolefin chain reacts quantitatively with iodine to give PO-I.

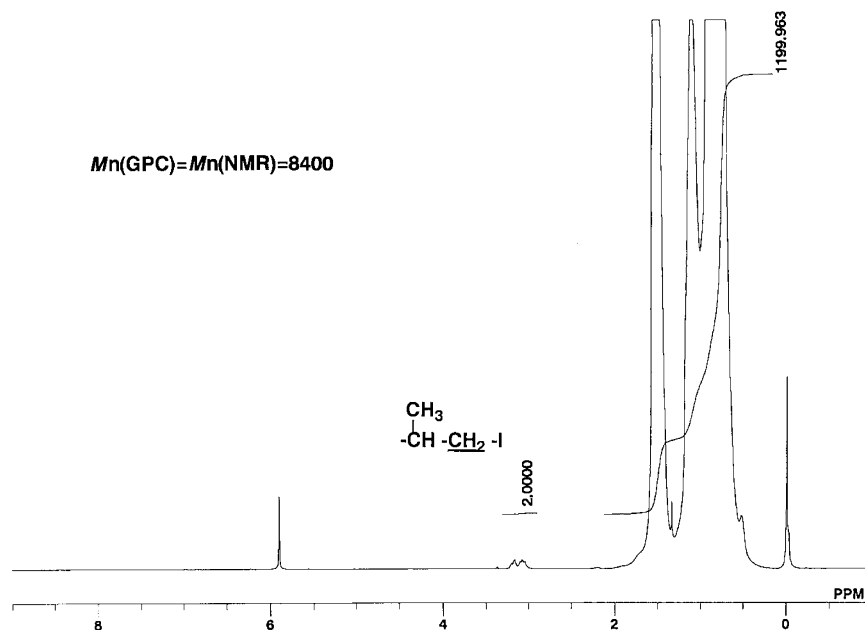


Figure 3. ^1H NMR spectrum of ataPP-I (run3).

Table III. Results of MMA copolymerization with PP-I *via* PP macroanion

Run	Polymer	Yield/mg	M_n	M_w/M_n
1	ataPP ($M_n = 8400, 35$ mg)	114	26000	1.21
		71.6	29500	1.10 (hex. insol.)
		42.4	23600	1.18 (hex. sol.)

Reaction condition: Run 1: toluene = 0.85 mL, ataPP-I = 4.2 μmol , Sm = 9 μmol , temp = 0°C, time = 3 min. Copolymerization condition: Run 1: MMA = 0.9 mmol, temp = 0°C, time = 1 h. Hexane soluble/insoluble fractionation condition: THF/hexane = 10/500 mL. M_n : Determined by GPC (THF at 40°C) using PS standards.

Reaction of the PO-I with Cp^*_2Sm and Block Copolymerization with MMA

The results of MMA copolymerization with ataPP-I are given in Table III.

Figure 4 shows GPC profiles of several polymer samples. The curve a) is the GPC curve of the ataPP-I. The curve b) corresponds to the block copolymer of PP with PMMA before washing with hexane, *i.e.*, the block copolymer is shifted toward higher molecular weight field and exhibits small shoulder. The GPC curve of the PP-*block*-PMMA after washing with hexane (curve c), *i.e.*, hexane insoluble) shows a narrower MWD with very little shoulder.

Figure 5 shows 68 MHz ^{13}C NMR spectrum of the PP-*b*-PMMA before (Figure 5a) and after washing with hexane (Figure 5b). The content of PP in the block copolymer after washing with hexane is lower than the that of PP before washing with hexane. (^{13}C NMR spectrum analysis confirms that the block copolymer is composed of ataPP and synPMMA [$r_r = 0.87$] segments in 25 mol% : 75 mol% ratio.)

Therefore, the shoulder shown in the crude product of Figure 4b was mainly derived from not PMMA but

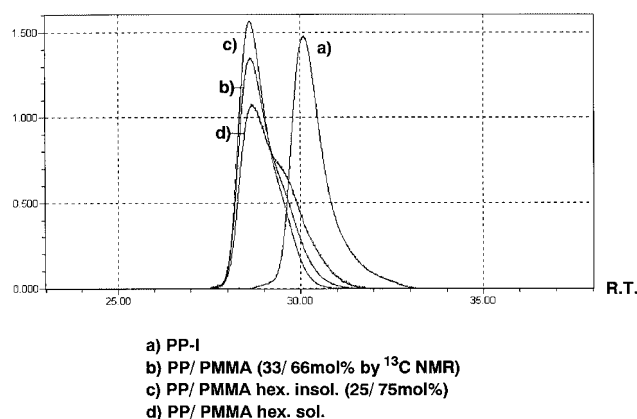


Figure 4. GPC profiles for ataPP-I, PP/PMMA before and after washing with hexane (run1).

PP homopolymer. Nomura *et al.* reported the presence of the coupling reaction of polymer-I with polymer-Sm- Cp^*_2 as a main side reaction.⁵

The iso poly(1-hexene)-I ($M_n = 4900$, MWD = 1.21) and isoPHx-*block*-synPMMA ($M_n = 8400/9300$, MWD = 1.19/1.09, before/after washing with hexane) were also produced.¹⁶

However, the preparation of synPP-*block*-synPMMA was not successful. In the case of synPP, the precipitation of the crystalline synPP-I took place. Synthesis of

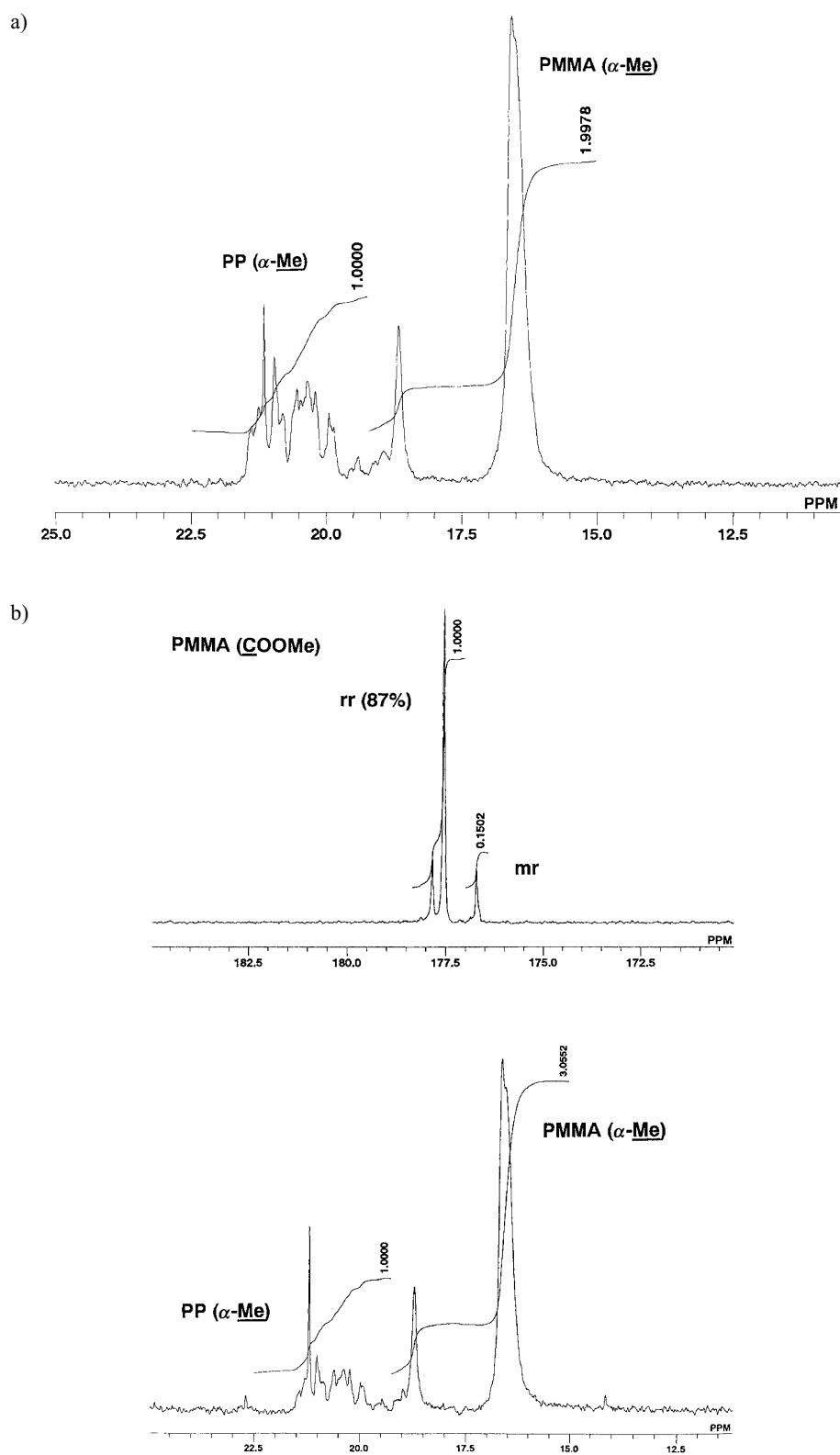


Figure 5. a) ^{13}C NMR spectrum of PP/PMMA before washing with hexane (run1). b) ^{13}C NMR spectrum of PP/PMMA after washing with hexane (run1).

higher molecular weight PO-*block*-PMMA and its application will be our future work.

CONCLUSIONS

The reactions of methyl methacrylate (MMA) or I₂ with the living zirconium-polyolefin bond (Zr-PO) using zirconocene catalyst system were conducted. Although the reaction of MMA with the living Zr-PP end do not proceed, iodine readily reacts with the living Zr-PO end, such as ataPP, iso poly(1-hexene) and synPP, quantitatively to give the terminal iodized polyolefin (PO-I).

Moreover, PO-PMMA block copolymers could be obtained by the reaction of MMA with living Sm-PO, which was formerly prepared by the transformation of PO-I by Cp*₂Sm. Direct block copolymerization of living PO with MMA are under investigation.

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14. Reaction of living poly(1-hexene) with MMA (8 mmol) for 13 h was also conducted ($M_n = 6700$, MWD = 1.04). ¹H NMR spectrum was poly(1-hexene) homopolymer.
15. Polymerization of 1-hexene for 65 h was also conducted ($M_n = 12100$, MWD = 1.06). The M_n of the PHx increased with increasing polymerization time and MWD was narrow. Therefore, the living nature of poly(1-hexene) was kept at longer polymerization time.
16. The ataPP-I ($M_n = 14000$, MWD = 1.09) and ataPP-*block*-synPMMA ($M_n = 20000$, MWD = 1.16) were also obtained.