Support Information

Facile Functionalization of Isotactic Polypropylene via Click Chemistry

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CONTENTS

Materials and general experimental methods S3-S7
Fig. S1 Synthetic route of three comonomers PAB, MAU, and SAO······S8
Fig. S2 ¹ H spectrum of MAU comonomer S8
Fig. S3 ¹³ C NMR spectrum of MAU comonomer
Fig. S4 ¹ H NMR spectrum of 11-alkynyl-1-decene comonomerS9
Fig. S5 ¹³ C NMR spectrum of 11-alkynyl-1-decene comonmer·····S10
Fig. S6 ¹³ C NMR spectrum of polypropylene·····S10
Fig. S7 GPC curve of different kind of copolymers
Fig. S8 ¹ H NMR spectrum of propylene/MAU copolymer·····S11
Fig. S9 ¹ H NMR spectrum of propylene/MD copolymer·····S12
Fig. S10 ¹ H NMR spectrum of SAO comonomerS12
Fig. S11 ¹³ C NMR spectrum of SAO comonomer S13
Fig. S12 ¹ H NMR spectrum of propylene/SAO copolymer·····S13
Fig. S13 ¹ H NMR spectrum of PAB comonomer
Fig. S14 ¹³ C NMR spectrum of PAB comonomer
Fig. S15 ¹ H NMR spectra of propylene/PAB copolymer·····S14
Fig. S16 Reactivity ratio of propylene/SAO copolymerization by Fineman-Ross methodS15

Fig. S17 Reactivity ratio of propylene/PAB copolymer by Fineman-Ross method
Fig. S18 ¹³ C NMR and Dept 135 of propylene/12-(dimethyl)(trimethylsilyalkynyl)silyl-
n-dodecane S16
Fig. S19 ¹ H-NMR spectrum of propylene/PAB-g-PEG······S17
Fig. S20 ¹ H-NMR spectrum of propylene/MAU-g-PEG······S17
Fig. S21 FT-IR spectrum for propylene/PAB-g-PEG······S18
Fig. S22 TGA curve of propylene/PAB-g-PEG······S18
Fig. S23 DSC curve of propylene/MAU-g-PEG······S18
Fig. S24 In-situ ¹ H-NMR spectra of PAB (after deprotection TMS)/PEG-N ₃ /CuBr/PMDETA reaction system
Fig. S25 In-situ ¹ H-NMR spectra of reaction among PAB/PEG-N ₃ /CuBr/PMDETA by adding raw materials simultaneously
Fig. S26 FT-IR spectrum for –SCH ₂ COOH modified propylene/PAB······S20
Fig. S27 ¹ H-NMR spectrum of hydroxybenzenethiol modified P/PAB copolymer······S20
Fig. S28 FTIR spectrum of hydroxybenzenethiol modified P/PAB copolymer······S21
Fig. S29 In-situ ¹ H-NMR spectra in CDCl ₃ of reaction among PAB/HSCH ₂ COOH······S21
Fig. S30 Volume variation of PP-g-PEG sample after swelling in water for different time·····S21
Fig. S31 The APCI-HRMS of MAU comonome S21
Fig. S32 The APCI-HRMS of MD comonomer S22
Fig. S33 The APCI-HRMS of SAO comonomer S22
Fig. S34 The APCI-HRMS of PAB comonomer S23
Fig. 35 In-situ ¹ H-NMR experiment for the Zr catalytic in $C_6D_5CD_3$ at 25 °C under N_2 S23 Table S1 Propylene/SAO copolymerization results for reactivity ratio calculationS24
Table S2 Propylene/PAB copolymerization results for reactivity ratio calculation S24
Reference S25

Materials and General Experimental Methods:

All moisture and/or oxygen sensitive manipulations were carried out using standard Schlenk techniques or in an Mbraun glovebox under a dry nitrogen atmosphere. Anhydrous solvents used in this work were purified by a solvent purification system (Etelux SPS). Commercial propylene was used after flowing through a purification column ($O_2 \le 0.1$ ppm, $H_2O \le 0.1$ ppm, $CO_2 \le 0.1$ ppm). Triisobutylaluminum (AlⁱBu₃) and trityltetrakis(pentauorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$) were purchased from Acros and Aldrich, respectively, and used as received. Methoxypoly(ethylene glycol) (PEG-OH) (M_w = 1900 or 4000 Da) was purchased from Sigma and dried under vacuum at 60 °C for 12 h before use. N, N, N', N", N"-pentamethyldiethylenetriamine (PMDETA) and copper bromide (CuBr) were obtained from Aldrich, and were used without further purification. Tetrabutylammoniumfluoride (TBAF, 1.0 M) in tetrahydrofuran was purchased from Acros. Trimethylsilylmethyllithium in hexane was obtained from Acros. Butylphenylacetylene was purchased from Alfa and used as received. All other reagents and solvents employed in this work are commercial available without any special requirement. Azido-terminated poly(ethylene oxide) (PEG-N₃) was synthesized according to the reported methods.^{1,2} The metallocene zirconium catalyst $\{Me_2Si(2,5-Me_2-3-(2-MePh)cyclopento[2,3-b]thiophen-6-yl)_2\}$ ZrCl₂(*rac* : *meso* = 1:1) employed in this contribution was synthesized according to the literature except using Eaton's reagent replacing super polyphosphoric acid in the Zr catalyst synthesis.³ ¹H and ¹³C NMR spectra of the catalyst and comonomers were recorded on a Bruker-400MHz spectrometer at ambient temperature, with CD_2Cl_2 (without internal reference), $CDCl_3$ (with trimethylsilyl as the internal reference) or C_6D_6 (without internal reference) as the solvent. Moreover, ¹H and ¹³C NMR spectra of polymer samples were obtained on the same Bruker-400MHz spectrometer at 120 °C, with o-C₆D₄Cl₂ (without internal reference) or C₂D₂Cl₄ (without internal reference) as the solvent. The weight-average molecular weight (M_w) and molecular weight distributions (PDI) of polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature gel permeation chromatograph (GPC). 1, 2, 4-Trichlorobenzene (TCB) was chosen as the eluting solvent at a flow rate of 1.0 mL/min and the calibration was made by polystyrene standard Easi-Cal PS-1 (PL Ltd). The melting (T_m) and crystallization temperatures (T_c) of the polymer samples were measured by differential scanning calorimetry (DSC, TA instruments, Model Q2000) under nitrogen atmosphere. The heating and cooling rates were 10 °C/min, ranging from -50 to 200 °C, and T_m was obtained from the second heating curve. Thermogravimetric analysis (TGA) was conducted under a nitrogen flow using thermogravimetric analyzer (TA instruments, Model Q50) with a heating rate of 10 °C /min. The HRMS was tested on a Bruke-Solanx 70 FT-MS with APCI as the ion source. The FT-IR spectra were taken on a Bio-Rad FTS-135 spectrophotometer using polymer thin films, made by hot pressing at 140 °C for 3 min. Swelling experiments were went on by soaking a rectangular specimen (about 7.26 × 3.19 × 0.24 mm) into deionized water for desired time, then measured its size with a vernier caplier (0.01 nm precision).

Synthesis of 11-(trimethylsilylalkynyl)-1-undecene (MAU). The syntheses of comonomers can be seen in Fig. S1. A solution of n-butyllithium in hexane (2.5 M, 96 mL, 240 mmol) was added to a solution containing trimethylsilylacetylene (23.57 g, 240 mmol) and anhydrous tetrahydrofuran (THF, 300 mL) at -78 °C. The mixture was stirred for an additional 4 h at -78 °C. Then, another solution containing 11-iodide-1-undecene (280.29 g, 200 mmol),⁴ and hexamethylphosphoramide (HMPA) (53.76 g, 300 mmol), diluted with THF (100 mL) was slowly added to the alkynyl lithium solution at -78 °C. After addition, the reaction system was allowed to room temperature and stirred for 12 h. The reaction mixture was guenched with water, and extracted with diethyl ether (2×100) mL). The combined organic layer was dried over magnesium sulfate, filtered, and then the solvents were removed under vacuum. The crude product was purified by column chromatography using hexane as the eluting agent and recrystallized at -30 °C. The final pure colorless liquid (35.00 g, yield \sim 70%) was further dried over magnesium sulfate, then filtered under vacuum before distilled. The pure MAU comonomer was stored at -30 °C under nitrogen atmosphere for polymerization. ¹H NMR (400 MHz, δ , ppm, C₆D₆): 5.78 (m, 1H), 5.01 (dd, J = 19.1 Hz, 13.7 Hz, 2H), 2.08 (t, J = 7.0Hz, 2H), 1.98 (q, 2H), 1.50-1.05 (m, 14H), 0.20 (s, 9H). ¹³C NMR (101 MHz, δ, ppm, C₆D₆): 139.03, 114.34, 107.81, 84.34, 34.04, 29.62, 29.30, 29.25, 29.16, 28.94, 28.78, 20.02, 0.21.

Synthesis of 11-alkynyl-1-undecene. A solution of TBAF in THF (1.0 M, 0.6 mL, 0.6 mmol) was added to a solution containing 11-(trimethylsilylalkynyl)-1-undecene (prepared above) (1.00 g,

4 mmol) and anhydrous tetrahydrofuran (THF, 10 mL) at room temperature. Then, the solution was stirred at room temperature for another 6 h. The reaction mixture was extracted with diethyl ether (2 × 100 mL). The combined organic layer was dried over magnesium sulfate, filtered, and then the solvents were removed under vacuum. The crude product was purified by column chromatography using hexane as the eluting agent. The final pure colorless liquid (0.65 g, 90%) was further dried over magnesium sulfate, then filtered under vacuum before distilled. The pure comonomer was stored at -30 °C under nitrogen atmosphere for polymerization. ¹H NMR (400 MHz, δ , ppm, CDCl₃): 5.88-5.72 (m, 1H), 4.96 (dd, *J* = 24.8 Hz, 13.6 Hz, 2H), 2.17 (td, *J* = 7.0, 2.3 Hz, 2H), 2.03 (m, 2H), 1.58-1.46 (m, 2H), 1.44-1.15 (m, 12H). ¹³C NMR (101 MHz, δ , ppm, CDCl₃): 139.14, 114.12, 84.67, 68.05, 33.81, 29.48, 29.11 (d, *J* = 13.0 Hz), 28.93, 28.76, 28.50, 18.40.

Synthesis of 8-(dimethyl)(trimethylsilylalkynyl)silyl-1-octene (SAO). Platinum(0)-1, 3divinyl-1, 1, 3, 3-tetramethyldisiloxane (1 mL, 2 wt%) catalyst was added to a solution containing 1, 7-octadiene (55.10 g, 500 mmol) and anhydrous methyl cyclohexane (65 mL) at room temperature, activated for 1 h. After the activation, chlorodimethylsilane (47.00 g, 500 mmol), diluted with methyl cyclohexane (150 mL) was slowly added, then further stirred at room temperature for 12 h. After that, the solvent was removed under vacuum. A solution of n-butyllithium in hexane (2.4 M, 234 mL, 562 mmol) was added to a solution containing trimethylsilylacetylene (55.20 g, 562 mmol) and anhydrous tetrahydrofuran (THF, 300 mL) at -78 °C. The mixture was stirred for an extra 4 h at -78 °C. After completion, the alkynyl lithium was added to the first reaction flask at room temperature, and stirred for another 12 h. The reaction mixture was quenched with water, and the resulting slurry was filtered. The filtrate was extracted with diethyl ether, dried over magnesium sulfate, filtered, and then the solvents were removed under vacuum. The crude product was purified by column chromatography using hexane as the eluting agent and recrystallized at -30 °C to give colorless oil product (66.00 g, yield 50%). The pure SAO was further dried over magnesium sulfate, then filtered under vacuum before distilled. The final SAO comonomer was stored at -30 °C under nitrogen atmosphere for polymerization. ¹H NMR (400 MHz, δ, ppm, C₆D₆): 5.63 (m, 1H), 4.86 (m, 2H), 1.83 (dd, J = 13.9, 6.8 Hz, 2H), 1.35-0.97 (m, 8H), 0.45 (m, 2H), 0.008 (m, 15H). ¹³C NMR (101 MHz, δ , ppm, C₆D₆): 139.37, 114.72, 113.77, 34.43, 33.58, 29.34 (d, J = 9 Hz), 24.33, 16.53, 0.21, -1.37.

Synthesis of 12-(dimethyl)(trimethylsilylalkynyl)silyl-1-dodecane. The process for synthesis of 12-(dimethyl)(trimethylsilylalkynyl)silyl-1-dodecane is similar to that of SAO, except using dodecene instead of 1,7-octadiene. ¹H NMR (400 MHz, δ , ppm, C₆D₆): 1.40-1.01 (m, 20H), 0.75 (t, J = 6.8 Hz, 3H), 0.49 (m, 2H), 0.07-0.01 (m, 15H). ¹³C NMR (101 MHz, δ , ppm, C₆D₆): 114.80, 113.81, 33.87 (d, J = 5.2Hz), 32.54, 30.33 (dd, J = 3.8, 3.7 Hz), 30.02, 24.39 (d, J = 11.0 Hz), 23.30, 16.52 (d, J = 17.3 Hz), 14.56, 0.21, -1.35.

Synthesis of 4-[4-(trimethylsilylalkynyl)-phenyl]-1-butylene (PAB). A solution of allylmagnesium bromide in diethyl ether (1.0 M, 120 mmol, 120 mL) was added to a solution containing (25.00 g, 100 mmol) of 4-Bromobenzylbromide dissolved in anhydrous diethyl ether (200 mL) at 0 °C. Then, the mixture was allowed to warm to room temperature and stirred for an additional 5 h. The reaction mixture was slowly poured into water, and then the aqueous layer was extracted with diethyl ether (2×100 mL). The combined organic layer was dried over magnesium sulfate, and the solvent was evaporated under vacuum to give the faint yellow product (21.00 g, vield $\sim 100\%$ from thin column chromatography), which was used without further purification. A solution of 4-Butenyl bromobenzene (21.00 g, 100 mmol) in triethylamine (200 mL) was added by copper (I) iodide (0.19 g, 1 mol%) and Bis(triphenylphosphine)palladium(II)chloride (0.70 g, 1 mol%). After freeze-vacuum-thaw degassing for 3 times, degassed trimethylsilylacetylene (14.70 g, 150 mmol) was added. Subsequently, the mixutre was refluxed at 90 °C for 36 h. The resulting brown slurry was filtered, and the solid filter cake was washed with diethyl ether. The combined organic layer was concentrated under vacuum, then washed with water and dried with MgSO₄. The solvent was evaporated under vacuum to give the brown crude product. The crude product was purified by column chromatography using hexane as the eluting agent and recrystallized at -30 °C to give colorless oil product (18.20 g, yield 80%). The pure PAB was further dried with MgSO₄, then filtered under vacuum before distilled. The distilled pure comonomer was stored at -30 °C under nitrogen atmosphere for polymerization. ¹H NMR (400 MHz, δ , ppm, C₆D₆): 7.44 (d, J = 8.1 Hz, 2H), 6.75 (d, J = 8.2 Hz, 2H), 5.64 (m, 2H), 4.91 (m, 2H), 2.35 (t, 2H), 2.07 (g, 2H), 0.25 (s, 9H). ¹³C NMR (101 MHz, δ, ppm, C₆D₆): 142.74, 137.91, 132.37, 128.80, 121.41, 115.31, 106.37, 93.76, 35.48, 35.39, 0.21.

Synthesis of 12-trimethylsilyl-1-dodecene (MD). A solution containing 11-iodide-1-undecene

(26.16 g, 93 mmol) and anhydrous tetrahydrofuran (THF, 60 mL) was added by a solution of trimethylsilylmethyllithium in hexane (0.56 M, 200 mL, 112 mmol) at -78 °C. The mixture was stirred for an additional 1 h at -78 °C, then further stirred at room temperature over night. The reaction mixture was quenched with water, and the resulting solution was extracted with hexane, dried over magnesium sulfate, filtered, and then the solvents were removed under vacuum. The crude product was purified by column chromatography using hexane as the eluting agent. The pure MD was further dried over CaH₂, then filtered under vacuum before distilled. The final MD comonomer was stored at -30 °C under nitrogen atmosphere for polymerization. ¹H NMR (400 MHz, δ , ppm, CDCl₃): 5.82 (m, 1H), 4.96 (m, 2H), 2.07 (m, 2H), 1.43-1.18 (m, 16H), 0.49 (m, 2H), -0.026 (s, 9H). ¹³C NMR (101 MHz, δ , ppm, CDCl₃): 140.86, 115.72, 35.49, 35.30, 31.32, 31.26, 31.17, 31.06, 30.83, 30.62, 25.58, 18.34, -0.007.



Fig. S1 Synthetic route of three comonomers PAB, MAU, and SAO



Fig. S2 1 H spectrum of MAU comonomer in C₆D₆



Fig. S3 $^{\rm 13}C$ NMR spectrum of MAU comonomer in C_6D_6



Fig. S4 ¹H NMR spectrum of 11-alkynyl-1-decene comonomer in CDCl₃



Fig. S5 ¹³C NMR spectrum of 11-alkynyl-1-decene comonomer in CDCl₃



Fig. S6 ¹³C NMR spectrum of polypropylene in $C_2D_2Cl_4$ at 120 °C ([mmmm] = 98.0%)



Fig. S7 Representative GPC curve of different kind of copolymers: PP entry 1, Table 1; P/MAU ($M_w = 31.8 \times 10^4$ PDI = 2.53); P/SAO ($M_w = 26.4 \times 10^4$ PDI = 2.41); P/PAB ($M_w = 30.9 \times 10^4$ PDI = 2.49)



Fig. S8 ¹H NMR spectrum of propylene/MAU copolymer (MAU = 1.68 mol%, entry 5 in Table 1)



Fig. S9 ¹H NMR spectrum of propylene/MD copolymer (MD = 3.73 mol%, entry 9 in Table 1)



Fig. S10 ¹H NMR spectrum of SAO comonomer in C_6D_6



Fig. S11 ¹³C NMR spectrum of SAO comonomer in C₆D₆



Fig. S12 Typical ¹H NMR spectrum of propylene/SAO copolymer (SAO mol% = 2.01 mol%, entry 10 in Table 1) in $C_2D_2Cl_4$ at 120 °C



Fig. S13 ¹H NMR spectrum of PAB comonomer in C_6D_6 (The peak labeled "*" was referred to the C_6D_6 solvent)



Fig. S14. ¹³C NMR spectrum of PAB comonomer in C₆D₆



Fig. S15 ¹H-NMR spectrum of propylene/PAB copolymer (PAB mol% = 1.27 mol%, entry 12 in Table 1) in C₂D₂Cl₄ at 120 °C.



Fig. S16 Calculated reactivity ratio of propylene/SAO copolymerization by Fineman-Ross method. G = -17.363F - 0.02183



Fig. S17 Calculated reactivity ratio of propylene/PAB copolymerization by Fineman-Ross method. G = -23.274F - 0.170



Fig. S18 ¹³C NMR spectra: (a) ¹³C NMR spectrum of 12-(dimethyl)(trimethylsilylalkynyl)silyln-dodecane; (b) Dept 135 spectrum of 12-(dimethyl)(trimethylsilylalkynyl)silyl-n-dodecane; (c)¹³C NMR spectrum of 12-(dimethyl)(trimethylsilylalkynyl)silyl-n-dodecane after treated with TBAF; (d) Dept 135 spectrum of 12-(dimethyl)(trimethylsilylalkynyl)silyl-n-dodecane after treated with TBAF.

The propylene/SAO copolymers were not used in such deprotection reaction and following click reaction, considering removal of alkynyl. To clarify this point, a simplified monomer 12-(dimethyl)(trimethylsilyalkynyl)silyl-n-dodecane was synthesized and put into this deprotection reaction. As shown in Fig. S18, compared the characterization results of ¹³C NMR and Dept 135 of starting materials with those of purified TABF treated product, the typical reasonance signal of alkynyl cannot be found in the product and a sharp peak in the ¹⁹F NMR appeared. Therefore, we think 12-(F)(dimethyl)silyl-n-dodecane was formed, resulting from F⁻ attacking the dimethylsilyl. Perhaps in other conditions the protected group can be regio-selectively removed.



Fig. S19 (a) propylene/PAB copolymer (PAB mol% = 2.42 mol%, $M_w = 43.5 \times 10^4$, PDI = 2.32); (b) propylene/PAB without protected TMS substitute; (c) propylene/PAB-g-PEG, synthesized in one pot. The volume fraction in theory of PP backbone (φ^t_{bb}) is calculated by $\varphi^t_{bb} = 4200/[4200 + (y + 113.14) \cdot x]$. ^cWeight fraction calculated by ¹H-NMR of the PP backbone is according to $\varphi^c_{bb} = \{[7I_{(2.00-0.64)ppm} + 3.50I_{(7.72-7.86)ppm}] + [11I_{(3.51-3.95)ppm} + 86.07I_{(7.22-7.86)ppm}], I_{(a-b)}$ means the integral area between a to b ppm in ¹H-NMR spectra of PP-g-PEG sample



Fig. S20 (a) propylene/MAU copolymer (MAU mol% = 3.49 mol%, entry 8, in Table 1); (b) propylene/MAU without protected TMS substitute; (c) propylene/MAU-g-PEG, synthesized in one pot



Fig. S21 FT-IR spectrum for propylene/PAB-*g*-PEG (PAB mol% = 2.42 mol%, propylene/PAB copolymer $M_w = 43.5 \times 10^4$, PDI = 2.32)



Fig. S22 TGA curve of propylene/PAB-g-PEG (PAB mol% = 2.42 mol%, propylene/PAB copolymer $M_w = 43.5 \times 10^4$, PDI = 2.32)



Fig. S23 DSC curves (second heating curve): (a) propylene/MAU copolymer (MAU mol% = 3.49 mol%); (b) propylene/MAU-g-PEG



Fig. S24 In-situ spectra in CDCl₃ of PAB (after deprotection TMS)/PEG-N₃/CuBr/PMDETA reaction system



Fig. S25 In-situ ¹H-NMR spectra in CDCl₃ of reaction among [PAB]/PEG-N₃/CuBr/PMDETA by adding raw materials simultaneously



Fig. S26 FT-IR spectrum for $-SCH_2COOH$ modified propylene/PAB (PAB mol% = 2.42 mol%, propylene/PAB copolymer $M_w = 43.5 \times 10^4$, PDI = 2.32)



Fig. S27 ¹H-NMR spectrum of hydroxybenzenethiol modified P/PAB copolymer (entry 12 in Table 1)



Fig. S28 FTIR spectrum: (a) propylene/PAB copolymer (comonomer incorporation 1.27%, entry 12 in Table 1); (b) hydroxybenzenethiol modified P/PAB copolymer (entry 12 in Table 1)



Fig. S29 In-situ ¹H-NMR spectra in CDCl₃ of reaction among PAB/HSCH₂COOH



Fig. S30 Volume variation after swelling for different time (PP-g-2.42PEG_{4k})



The theoretical molecular weight of MAU comonomer ($C_{16}H_{30}Si$) was 250 and calculated molecular weight was 250.15.





The theoretical molecular weight of MD comonomer ($C_{15}H_{32}Si$) was 240, and calculated molecular weight was 240.19.



Fig. S32 The APCI HRMS result of MD comonomer

The theoretical molecular weight of SAO comonomer ($C_{15}H_{30}Si_2$) was 266, and calculated molecular weight was 266.18.

Fig. S33 The APCI-HRMS test of SAO comonomer



The theoretical molecular weight of PAB comonomer ($C_{15}H_{20}Si$) was 228, and calculated molecular weight was 228.15.



Fig. S34 The APCI-HRMS test of PAB comonomer

Fig. 35 In-situ ¹H-NMR experiment for the Zr catalytic system in $C_6D_5CD_3$ at 25 °C under nitrogen atmosphere: [Zr] = catalyst **c**, [B] = [Ph₃C][B(C₆F₅)₄], [Zr]=10 umol, [B] = 11 umol, [Al^{*i*}Bu₃] = 15 umol, [MAU] = [SAO] = [PAB] = 20 umol, $C_6D_5CD_3 = 0.5$ mL.

Entry	SAO (mmol/L)	Incorp. ^b (mol%)	X ^c (P/SAO)	Y ^d (dP/dSAO)	G (X(1-Y)/Y)	F (X ² /Y)
1	120	6.72	0.739	13.881	-0.686	0.0393
2	110	6.10	0.806	15.393	-0.754	0.0422
3	90	4.98	0.986	19.080	-0.934	0.0510
4	80	4.62	1.108	20.645	-1.054	0.0595
5	60	3.58	1.478	26.933	-1.423	0.0811

Table S1 Propylene/SAO copolymerization with different comonomer concentration^a

^{*a*}Conditions: catalyst 5 µmol, [Ph₃C][B(C₆F₅)₄] 10 µmol, Al^{*i*}Bu₃ = 0.5 mmol, propylene 1 atm, $V_{total} = 30$ mL, reaction for different time. ^{*b*}Comonomer incorporation (mol%) established by ¹H NMR spectra at 120 °C with C₂D₂Cl₄ as a solvent. ^{*c*}The molecular ratio of propylene and [SAO] comonomer in feed, [P] = 0.0887 mol/L. ^{*d*}The molecular ratio of propylene and [SAO] in copolymers.

Entry	[PAB] (mmol/L)	Incorp. ^b (mol%)	X ^c ([P]/[PAB])	Y ^d (d[P]/d[PAB])	G (X(1-Y)/Y)	F (X²/Y)
1	60	2.43	1.478	40.152	-1.441	0.0544
2	80	3.09	1.108	31.362	-1.073	0.0391
3	90	3.37	0.986	28.674	-0.952	0.0339
4	100	3.57	0.887	27.011	-0.854	0.0291
5	110	3.82	0.806	25.178	-0.774	0.0258

Table S2 Propylene/[PAB] copolymerization with different comonomer cocentration^a

^{*a*}Conditions: catalyst 5 µmol, $[Ph_3C][B(C_6F_5)_4]$ 10 µmol, propylene 1 atm, $V_{total} = 30$ mL, reaction for different time. ^{*b*}Comonomer incorporation (mol%) established by ¹H NMR spectra at 120 °C with C₂D₂Cl₄ as a solvent. ^{*c*}The molecular ratio of propylene and [PAB] comonomer in feed, [P] = 0.0887 mol/L. ^{*d*}The molecular ratio of propylene and [PAB] in copolymers.

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