

Supporting Information

Efficient Synthesis of Diverse Well-defined Functional Polypropylenes with High Molecular Weights and High Functional Group Contents via Thiol-halogen Click Chemistry

Xiao-Yan Wang,^{ab} Yan-Guo Li,^a Hong-Liang Mu,^a Li Pan,^{*c} Yue-Sheng Li^{*ac}

^aState Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: ysli@ciac.jl.cn

^bUniversity of Chinese Academy of Sciences, Changchun Branch, Changchun 130022, China

^cSchool of Material Science and Engineering, Tianjin University, Tianjin 300072, China. E-mail: lilypan78@yahoo.com

Experimental section

General procedure and materials

All work involving air- and/or moisture-sensitive compounds was carried out under a nitrogen atmosphere by using standard Schlenk technique. The molecular weights and the molecular weight distributions of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature gel permeation chromatography. 1,2,4-trichlorobenzene (TCB) was employed as the 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 FT-IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. The ¹H NMR data of polymer samples were obtained on a Bruker 400 MHz spectrometer at 125 °C with *o*-C₆D₄Cl₂ or C₂D₄Cl₂ as the solvent. The IUD contents of the copolymer samples were determined by ¹H NMR spectra and calculated according to the formula: IUD mol% = [6I_{3.12-3.27ppm}/(2I_{0.90-2.07ppm} - 13I_{3.12-3.27ppm})] × 100%, where I_{xppm} is the peak integral of proton at x ppm. The CIUD and BrUD contents of the copolymers are determined *via* the similar method. The PLLA and PCL contents of the graft copolymer samples were determined by ¹H NMR spectra and calculated according to the formulas: PLLA wt% = $M_{LLA}I_{5.26-5.46ppm} / [M_{LLA}I_{5.26-5.46ppm} + M_P(I_{0.90-1.99ppm} - 3I_{5.26-5.46ppm})/6] \times 100\%$, PCL wt.% = $M_{CL}(I_{4.15-4.53ppm} + I_{3.75-3.91ppm}) / [M_{CL}(I_{4.15-4.53ppm} + I_{3.75-3.91ppm}) + M_P(I_{0.87-2.17ppm} - 3I_{4.15-4.53ppm})/3] \times 100\%$. The M_n s of PCL-PhSH were determined by ¹H NMR spectra and calculated according to the formula: $M_n(\text{PCL-PhSH}) = M_{CL}I_{3.99-4.15ppm} / I_{3.60-3.70ppm}$. The M_n s of PCL-RSH were calculated by the similar method. The molecular weight distributions of the PCL samples were determined at 35 °C by a waters 1525 type gel permeation chromatography. The DSC measurements

were performed on a Perkin-Elmer Pyris 1 differential scanning calorimeter at a rate of 10 °C/min.

Novozyme 435 (CALB) was purchased from Aldrich and dried in a vacuum oven at 25 °C for 48 hours before use. L-lactide was purified by the repeated recrystallization from ethyl acetate solution, while ϵ -caprolactone was purified via distillation after dried over CaH_2 . Other materials were purchased and used without further purification. The halogenated polypropylenes were prepared following the procedure reported by our group.^{1,2}

Thiol-halogen nucleophilic substitution reactions to synthesize side group-functionalized *i*PPs

In a 50 mL schlenk flask, 50 mg halogenated copolymer suspended in 10 mL decalin at room temperature. The flask was heated to 80 °C for 20 min to make the copolymer dissolve as possible, and then cooled down to the room temperature. Then 5 mL *N,N*-dimethyl formamide was added as another solvent. After the addition of thiol (100 eq. of iodine) and triethylamine (100 eq. of iodine), the mixture was stirred at 50 °C for a certain period of time, followed by pouring into 100 mL ethanol and then filtered. The polymers were isolated, washed with ethanol and acetone for several times and then dried in vacuo at 30 °C to a constant weight.

The preparation of *i*PP-*g*-PLLA via graft-from approach

Following the aforementioned procedure, the hydroxyl-containing *i*PP initiator was prepared via the thiol-halogen reaction of propylene/IUD (3.53 mol% IUD) copolymer with 2-mercaptoethanol. To a 100 mL bottle, 100 mg fully dried hydroxylated polypropylene was added. After the addition of toluene and L-lactide (0.72 g, 5 mmol), the flask was heated to dissolve the polymer and then remained at 90 °C. The polymerization was started by the addition of SnOct_2 toluene solution ($\epsilon\text{-CL}:\text{SnOct}_2 = 2000:1$, mol/mol). The total volume of the reaction solution was 15 mL. After 1 h or 1.5 h, the polymerization was stopped by pouring into formic acid-acidized *n*-hexane. The polymer mass were isolated, washed with cold methanol and then extracted with hot THF in a Soxhlet apparatus for 24 h to remove any LLA homopolymer.

The synthesis of PCL-RSH and PCL-PhSH

2-Mercaptoethanol (240 μl , 3.40 mmol) and ϵ -caprolactone (5.5 mL, 50 mmol) were mixed in a screw cap reaction vial. Addition of 100 mg of Novozyme 435 started the reaction that was allowed to run at 70 °C for 12 h. The reaction was stopped by diluting the mixture with dichloromethane and then filtering out the enzyme. The PCL-RSH products were precipitated in cold methanol, isolated and washed with cold methanol. The successful synthesis of PCL-SH was evidenced by the comparison with literature ¹H and ¹³C NMR spectral data.³ The typical ¹H and ¹³C NMR spectra of the PCL-PhSH, which was prepared following the similar procedure were shown in Fig. S6.

The preparation of *i*PP-*g*-PCL via thiol-halogen coupling

In a 50 mL schlenk flask, 100 mg propylene/IUD copolymer (3.53 mol% IUD) suspended in 10 mL decalin at room temperature. The flask was heated to 80 °C for 20 min to make the copolymer dissolve as possible, and then cooled down to the room temperature. Then 15 mL N,N-dimethyl formamide was added as another solvent. After the addition of PCL-SH (10 eq. of iodine) and triethylamine (20 eq. of iodine), the mixture was stirred at 70 °C for 24 h. After removing the solvent under vacuum as much as possible, the products were precipitated in cold methanol. The polymer mass were isolated, washed with cold methanol. And then they were soaked in and washed with dichloromethane for many times to remove any ϵ -CL homopolymer.

The detailed analysis about the influence of halogen type on the reactivity of thiol-halogen reaction

The influence of halogen group type on the reactivity of thiol-halogen reaction was detailedly investigated by treating the copolymers produced by *rac*-Et(Ind)₂ZrCl₂ (Table 1, entries B1-3) with methyl mercaptoacetate under the same conditions. The halogenated salts as by-product, deriving from the thiol-halogen nucleophilic displacement reaction in the presence of triethylamines (Et₃N), could be easily removed by sublimation during the reaction or being washed off after the reaction in a very simple and effective procedure. For the propylene/IUD copolymer, the thiol-halogen reaction almost reached completion after stirring for 3 h at 50 °C (Table 2, entry 1), as illustrated by the ¹H NMR spectrum in Fig. S1. The peaks corresponding to the -CH₂I, originally at 3.20 ppm, are absent in the spectrum of the product, while new peaks at 3.72 ppm attributed to the formed methoxy in ester group can be clearly observed. For comparison, thiol-halogen nucleophilic substitution click reactions of methyl mercaptoacetate with propylene/BrUD and propylene/ClUD copolymers were also performed under the same conditions (Table 2, entries 2, 3). Different from the iodinated copolymers, the reactivity of brominated product is rather low. After reacting for 3 h, the most peaks attributed to -CH₂Br still remained in the ¹H NMR spectra of the product. Only small part of the brominated polypropylene was transformed into the functionalized product which displays the characteristic peak at 3.72 ppm corresponding to the formed methoxy in ester group. The degree of functionalization is only about 25%. Lower reactivity is probably caused by the poorer leaving ability of bromine group. For propylene/ClUD copolymer, after stirring for 3 h, the characteristic peaks in ¹H NMR spectra corresponding to the functional product were not detectable. It indicates that the chlorinated copolymer exhibits the lowest reactivity in contrast with iodinated and brominated copolymers. Therefore, upon treatment of copolymers containing different halogen groups with methyl mercaptoacetate, the order of C-X (halogen) reactivity in the thiol-halogen click chemistry can be clearly summarized as C-I >> C-Br > C-Cl bond, which is consistent with the leaving sequence of the halogen groups.

References

- [1] X. Y. Wang, Y. X. Wang, X. C. Shi, J. Y. Liu, C. L. Chen and Y. S. Li, *Macromolecules*, 2014, **47**, 552.
- [2] X. Y. Wang, Y. Y. Long, Y. X. Wang and Y. S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2014, DOI: 10.1002/pola.27409.
- [3] C. Hedfors, E. Östmark, E. Malmström, K. Hult and M. Martinelle, *Macromolecules*, 2005, **38**, 647.

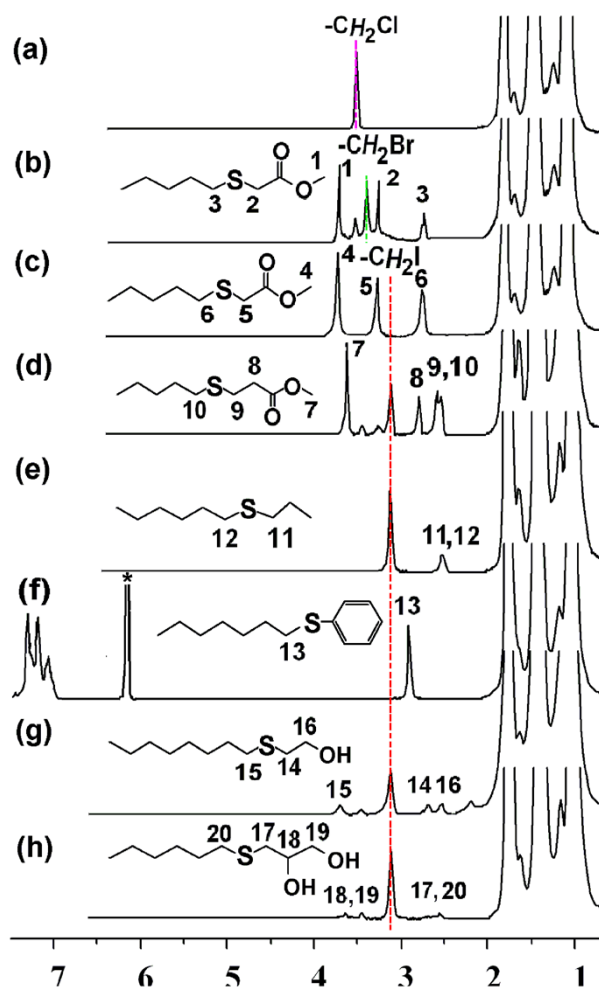


Fig. S1 ^1H NMR spectra ($o\text{-C}_6\text{D}_4\text{Cl}_2$, 125 °C) for products by thiol-halogen nucleophilic substitution click reaction for 3 h involving: (a) propylene/CIUD copolymer with $\text{SHCH}_2\text{COOCH}_3$ (Table 2, entry 3); (b) propylene/BrUD copolymer with $\text{SHCH}_2\text{COOCH}_3$ (Table 2, entry 2); (c) propylene/IUD copolymer with $\text{SHCH}_2\text{COOCH}_3$ (Table 2, entry 1); (d) propylene/IUD copolymer with $\text{SHCH}_2\text{CH}_2\text{COOCH}_3$ (Table 2, entry 4); (e) propylene/IUD copolymer with $\text{SHCH}_2\text{CH}_2\text{CH}_3$ (Table 2, entry 6); (g) propylene/IUD copolymer with $\text{SHCH}_2\text{CH}_2\text{OH}$ (Table 2, entry 5); (h) propylene/IUD copolymer with $\text{SHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ (Table 2, entry 7). (f) ^1H NMR spectra ($\text{C}_2\text{D}_4\text{Cl}_4$, 125 °C) for the product by thiol-halogen reaction of propylene/IUD copolymer with SHC_6H_5 for 2 h: (Table 2, entry 12). All the functionalized polypropylenes are derived from the copolymers obtained by $rac\text{-Et}(\text{Ind})_2\text{ZrCl}_2$ (Table 1, entries B1-B3).

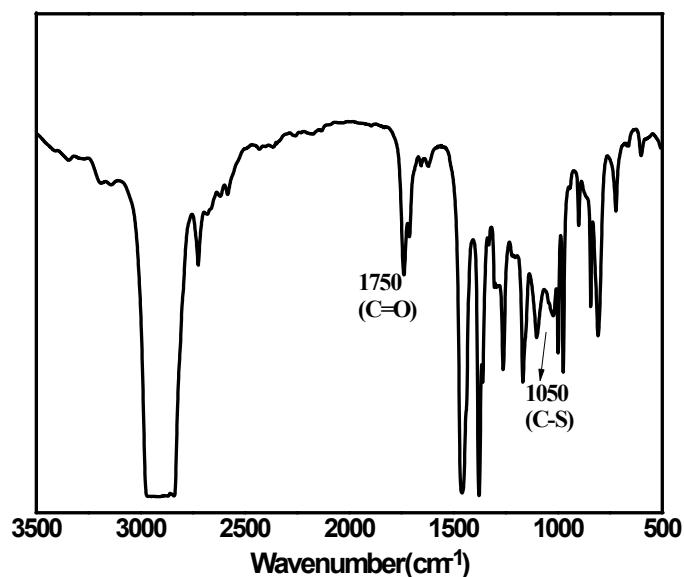


Fig. S2 FT-IR spectra for: mercaptoacetic acid functionalized polypropylene derived from the copolymer produced by (pyridyl-amido)hafnium catalyst containing 7.06 mol% IUD.

Fig. S3 GPC profiles for: (a) propylene/IUD copolymer (IUD mol% = 3.54%) before and after the thiol-halogen reaction with mercaptoethanol, solid line: $M_w = 141$ kg/mol with PDI = 1.81, dotted line: $M_w = 140$ kg/mol with PDI = 1.73; (b) propylene/IUD copolymer (IUD mol% = 7.06%) before and after the thiol-halogen reaction with methyl mercaptopropionate, solid line: $M_w = 120$ kg/mol with PDI = 1.92, dotted line: $M_w = 119$ kg/mol with PDI = 2.03; (c) propylene/IUD copolymer (IUD mol% = 11.0%) before and after the thiol-halogen reaction with thiophenol, solid line: $M_w = 108$ kg/mol with PDI = 2.13, dotted line: $M_w = 110$ kg/mol with PDI = 2.25. All the functional polymers are originated from poly(propylene-*co*-IUD)s produced by (pyridyl-amido)hafnium catalyst (Table 1, entries A1-A3).

Fig. S4 DSC profiles for: (a) propylene/IUD copolymer (IUD mol% = 3.54%) before and after the thiol-halogen reaction with mercaptoethanol, solid line: $T_m = 124$ °C, dotted line: $T_m = 124$ °C; (b) propylene/IUD copolymer (IUD mol% = 7.06%) before and after the thiol-halogen reaction with methyl mercaptopropionate, solid line: $T_m = 105$ °C, dotted line: $T_m = 106$ °C; (c) propylene/IUD copolymer (IUD mol% = 11.0%) before and after the thiol-halogen reaction with thiophenol, solid line: $T_m = 85$ °C, dotted line: $T_m = 86$ °C. All the functional polymers are originated from poly(propylene-*co*-IUD)s produced by (pyridyl-amido)hafnium catalyst (Table 1, entries A1-A3).

Fig. S5 FT-IR spectra for: (a) mercaptoethanol functionalized polypropylene; (b) *i*PP-*g*-PCL graft copolymers with 38.6 wt% of CL units; (c) *i*PP-*g*-PLLA graft copolymers with 34.5 wt% of LLA units. All the functional polymers are originated from poly(propylene-*co*-IUD)s produced by (pyridyl-amido)hafnium catalyst (IUD mol% = 3.54%, Table 1, entry A1).

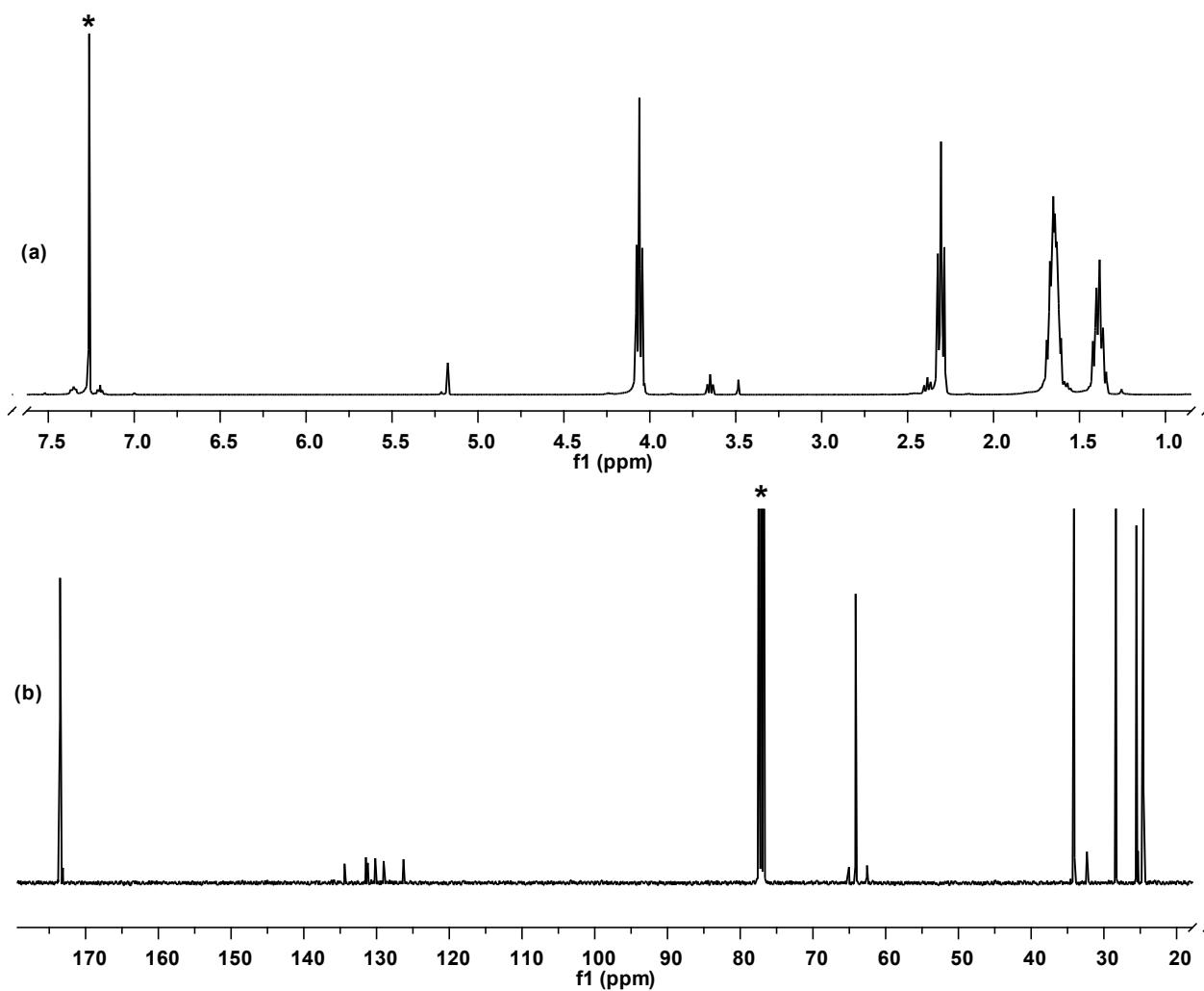


Fig. S6 (a) ¹H NMR spectrum (CD₃Cl, 25 °C) of PCL-PhSH; (b) ¹³C NMR spectrum (CD₃Cl, 25 °C) of PCL-PhSH.

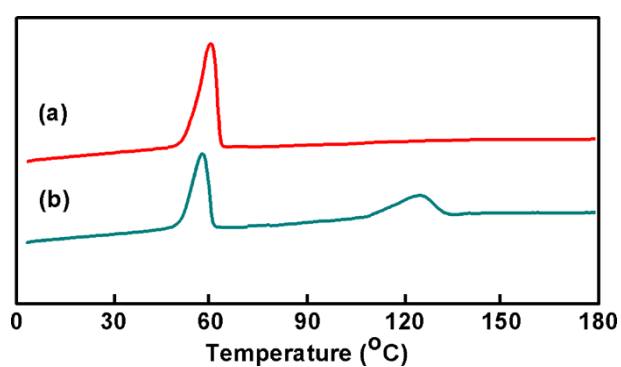


Fig. S7 The DSC curves (at a rate of 10 °C/min) for: (a) $T_m = 61$ °C (PCL-PhSH, $M_n = 2,070$ g/mol); (b) $T_{m1} = 59$ °C, $T_{m2} = 124$ °C (iodinated *i*PP/PCL-PhSH blends with 60 wt% of PCL).

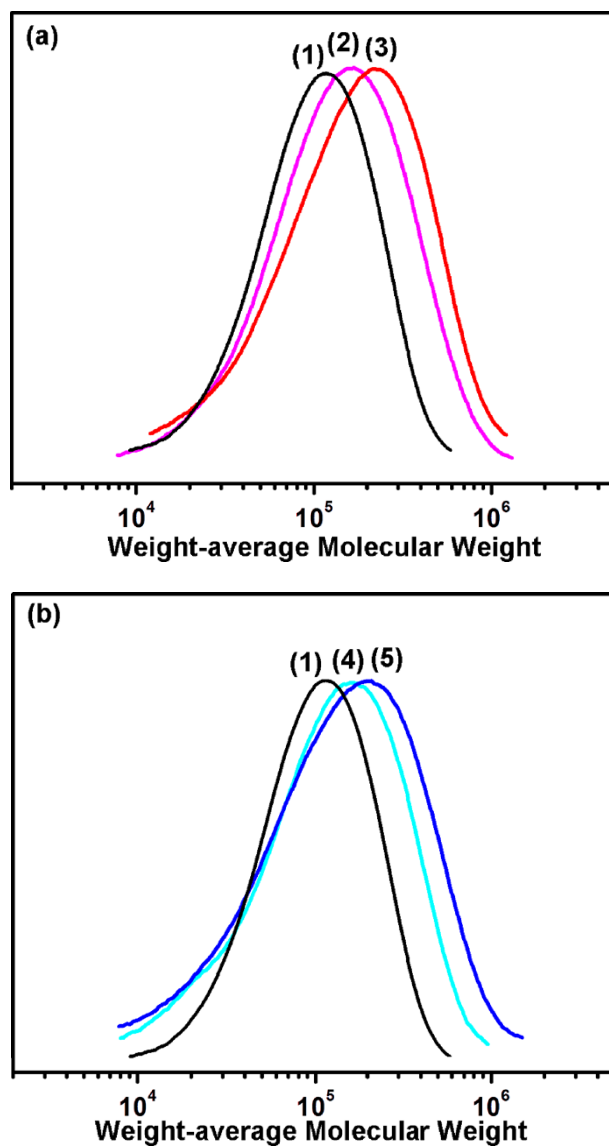


Fig. S8 (a) GPC profiles of (1) propylene/IUD copolymer (Table 1, entry A1, $M_w = 141$ kg/mol, PDI = 1.81), graft copolymers containing (2) 38.6 wt% PLLA ($M_w = 195$ kg/mol, PDI = 2.15) and (3) 71.7 wt% PLLA ($M_w = 229$ kg/mol, PDI = 2.42);

(b) GPC profiles of (1) propylene/IUD copolymer (Table 1, entry A1, $M_w = 141$ kg/mol, PDI = 1.81), graft copolymers containing (4) 34.5 wt.% PCL ($M_w = 175$ kg/mol, PDI = 2.43) and (5) 69.9 wt.% PCL ($M_w = 218$ kg/mol, PDI = 2.59).