# Polymer Chemistry

Accepted Manuscript

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/polymers

# 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]

[a]*State 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*

[b]*University of Chinese Academy of Sciences, Changchun Branch, Changchun 130022, China*

[c]*School of Material Science and Engineering, Tianjin University, Tianjin 300072, China. E-mail: lilypan78@yahoo.com*

† Electronic supplementary information (ESI) available. See DOI:

Polymer Chemistry Accepted Manuscript

**Abstract:** The thiol-halogen click chemistry between halogenated isotactic polypropylenes (*i*PPs) and thiols was systematically investigated for the first time. An order of the copolymers reactivity was summarized as iodinated >> brominated > chlorinated *i*PP, while for different thiols, the reactivity depended on not only the acidity of the sulfydryl but also the competition of the polar group in the thiols with -SH to participate in the nucleophilic substitution reaction. In this case, various polar groups including hydroxyl, ester, aryl, thiazolyl and amino have been successfully introduced into *i*PP in a quantitative way, by employing iodinated *i*PP as the highly reactive intermediate. The content of polar group in the high molecular weight functional *i*PPs ($M_w > 100$ kg/mol) could be tuned in a wide range of 0-11 mol%. More notably, this new strategy offers an effective avenue to prepare well-defined graft copolymer *i*PP-*g*-PCL from the halogen functionalized *i*PP and poly(ε-caprolactone)s with highly reactive -SH end (PCL-PhSH). Initiated by the resultant hydroxyl-containing *i*PP, the ring-opening polymerization of L-lactide (LLA) provided another kind of graft copolymer *i*PP-*g*-PLLA.

KEYWORDS: polyolefins; functionalization; click chemistry; graft copolymer; aliphatic polyesters

Polymer Chemistry Accepted Manuscript

Polymer Chemistry Accepted Manuscript

## Introduction

As one of the fastest growing thermoplastics, isotactic polypropylene (*i*PP) represents a quarter of commercial polymers produced in the world. It is widely used in commodity applications related to our everyday life, with a unique combination of chemical and physical properties, low cost as well as excellent processability and recyclability.[1-3] On the other hand, *i*PP is a kind of nonpolar polymer. The lack of polar groups poses serious problems in the application areas where adhesion, dyeability, printability, and compatibility with other polymers are paramount. Thus, there is a strong desire and a constant interest in the chemical modification (functionalization) of *i*PP to improve its poor interactive properties and broaden its applications to higher value products.[4-9] Thousands of reports and patents have discussed the functionalization approaches involving both direct[10-19] and postpolymerization[20-24] processes with limited industrial success. The rare availability of stereo-specific and heteroatom-resistant catalysts (direct process) as well as the stable structures of *i*PPs (post process) have posted huge technological barriers for finding an acceptable chemical route to prepare functional *i*PPs on a large-scale. In the past two decades, Chung and his colleagues precedently proposed a reactive polyolefin intermediate approach, which affords a new class of functional *i*PPs with high molecular weight and well-controlled molecular structures *via* the combination of metallocene catalysis and reactive comonomers.

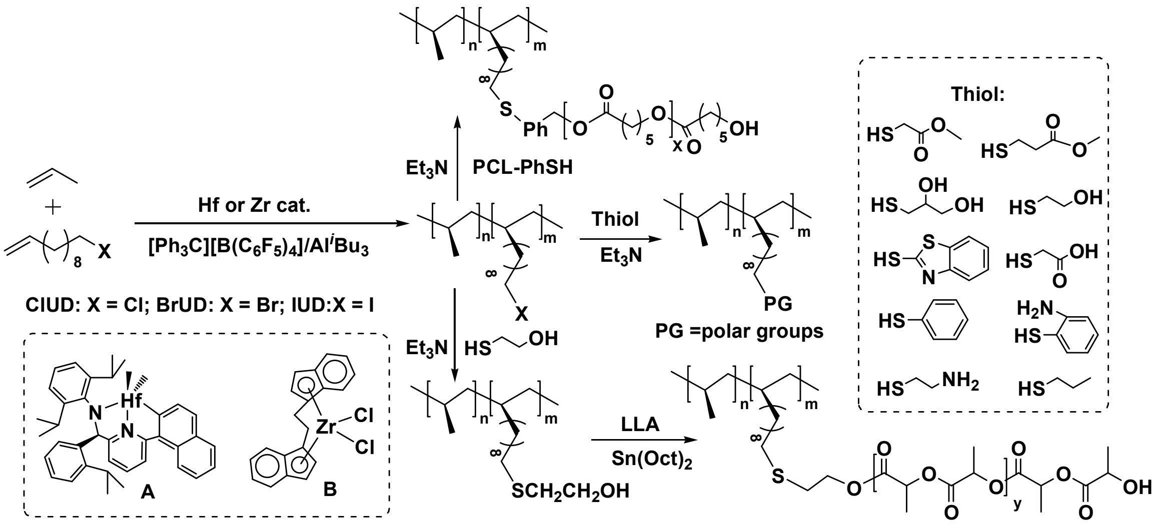
Promoted by Ziegler-Natta or zirconocene catalyst, a series of reactive polyolefin intermediates containing organoborane,[25-26] benzylic protons ($PhCH_3$),[27-31] styrene moieties[32-34] or halogen group[35-37] have been synthesized *via* the copolymerization of reactive comonomers with ethylene or propylene. Specific to the synthesis of polyolefin intermediate containing reactive halogen group, in addition to the olefin/ω-halo-α-alkenes copolymerization by Ziegler-Natta or zirconocene catalyst,[35-37] the ethylene (co)polymerization by late transition or rare earth metal catalyst provided polyethylene intermediates bearing end-capping 2-bromoisobutyryl,[38,39] iodine[40,41] and benzyl chloride groups.[42] The following facile macromolecule reactions produced various functional polyolefins. Ziegler-Natta catalysts usually produce the copolymers with a structure far from unity.

While, late transition or rare earth metal catalyst usually provided the end-functionalized polyolefins possessing low molecular weights ($M_w$ < 10 kg/mol). A great many metallocene catalysts can successfully produce reactive polyethylenes with high molecular weights ($M_w$ > 100 kg/mol) and reactive group content (> 5 mol%) as well as uniform molecular weight and composition distributions. However, only a few metallocene catalysts can promote the efficient isospecific copolymerization of propylene with some elaborately-designed reactive comonomers. The limited successful examples include the propylene/*p*-(3-butenyl)toluene and propylene/5-hexenyl-9-BBN (9-BBN: 9-borabicyclo[3.3.1]nonane) copolymerization mediated by *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph(Ind)]_2ZrCl_2$,[25,31] and the propylene/*p*-(3-butenylstyrene) copolymerization catalyzed by *rac*-$CH_2(3\text{-}t\text{-}Butyl\text{-}Ind)_2ZrCl_2$.[34] However, it is very difficult for these copolymerizations to produce well-defined reactive *i*PPs, in which molecular weight, reactive group content, tacticity and yield can simultaneously reach a satisfying level. Thus, it is extremely necessary to further develop greatly reactive *i*PP intermediate and efficient conversion strategy to provide diverse functional *i*PPs with high molecular weight and functional group content.

The convenient $S_N2$ nucleophilic substitution of reactive halogen groups by a wide range of thiols has recently been touted as efficient click chemistry, because of the facile operation, high reactivity, mild conditions and organic catalyst.[43-46] By far, however, its application in the field of functional polyolefins has seldom been reported.[47] Recently, we presented the detailed investigation about the stereospecific propylene/ω-halo-α-alkenes copolymerization by dimethyl(pyridyl-amido)hafnium and *rac*-$Et(Ind)_2ZrCl_2$ catalysts.[48, 49] In this paper, based on this copolymerization reaction and the thiol-halogen click chemistry, we synthesized a series of well-defined side-group functionalized polypropylenes possessing high molecular weights ($M_w$ > 100 kg/mol) and high functional group content (> 7 mol%) as well as high isotacticity ([mmmm] > 99%). The results fully display that the iodinated polypropylenes are highly reactive polymer intermediates and the thiol-halogen click chemistry is an efficient conversion strategy (Scheme 1). Moreover, graft copolymers with PP backbone and polyester graft chains (*i*PP-*g*-PCL and *i*PP-*g*-PLLA) were easily obtained through

Polymer Chemistry Accepted Manuscript

this efficient approach. Besides, the systematic investigation about the influence factors on the reactivity of thiol-halogen click chemistry was carried out in advance to better fulfill these works, since the relevant study involving polyolefin has not been reported yet.



**Scheme 1** Synthetic route of functional polypropylenes.

# Results and discussion

## The preparation of reactive polypropylenes containing pendent halogen groups

All the reactive polypropylenes containing pendent halogen groups were prepared in the bulk scale by using large reactor. Based on our previous investigations,[48,49] the propylene/11-iodo-1-alkene (IUD) copolymerizations were carried out using dimethyl (pyridyl-amido)hafnium catalyst (Cat. Hf, Table 1, entries A1-3) to prepare the reactive iodinated *i*PPs with high molecular weights ($M_w$ > 100 kg/mol) and high isotacticity ([mmmm] > 99%). While *rac*-Et(Ind)$_2$ZrCl$_2$ (Cat. Zr), which possesses superior tolerability towards halogen groups, was employed as the catalyst to prepare the polypropylenes containing pendent bromine and chlorine groups on a large scale (Table 1, entries B1-3).

Polymer Chemistry Accepted Manuscript

**Table 1** The data of propylene/ω-halo-α-alkene copolymerization[a]

| Ent. | Cat. (μmol) | Comon. (mL) | Yield (g) | Activity[b] | Incorp.[c] (mol %) | $M_w$[d] (kg/mol) | PDI[d] | $T_m$[e] (°C) |
|---|---|---|---|---|---|---|---|---|
| A1 | Hf (20) | IUD (1.5) | 4.40 | 0.88 | 3.54 | 141 | 1.81 | 124 |
| A2 | Hf (20) | IUD (3.0) | 3.18 | 0.64 | 7.06 | 120 | 1.92 | 105 |
| A3 | Hf (20) | IUD (4.5) | 2.07 | 0.41 | 11.0 | 108 | 2.13 | 85 |
| B1 | Zr (5) | ClUD (2.0) | 1.58 | 1.26 | 7.11 | 14.5 | 1.84 | — |
| B2 | Zr (5) | BrUD (2.0) | 2.34 | 1.87 | 7.20 | 16.2 | 1.88 | — |
| B3 | Zr (5) | IUD (2.0) | 3.03 | 2.40 | 7.38 | 22.9 | 1.64 | — |

[a] Set A: Cat. Hf 20 μmol, $[Ph_3C][B(C_6F_5)_4]$ 40 μmol, $Al(^iBu)_3$ 2.00 mmol, $V_{total}$ = 160 mL, propylene 1 atm, at 25 °C copolymerization for 15 min; Set B: Cat. Zr 5 μmol, $[Ph_3C][B(C_6F_5)_4]$ 10 μmol, $Al(^iBu)_3$ 0.50 mmol, $V_{total}$ = 40 mL, propylene 1 atm, at 25 °C copolymerization for 15 min. [b] Catalytic activity: kg polymer/mmol$_{Zr/Hf}$·h. [c] Comonomer incorporation (mol%) established by $^1$H NMR spectra. [d] Weight-average molecular weights and polydispersity indices determined by GPC at 150 °C in 1,2,4-$C_6Cl_3H_3$ *vs.* narrow polystyrene standards. [e] Melting temperature determined by DSC at a rate of 10 °C/min.

## Reactivity towards thiol-halogen nucleophilic substitution click chemistry

We have demonstrated that carboxylate group could be efficiently introduced into *i*PP *via* the thiol-halogen reaction of poly(propylene-co-IUD)s with methyl mercaptoacetate.[48] In following work, we made the most of this strategy to prepare diverse functional polypropylenes *via* the reaction between the reactive polypropylenes containing different halogen groups and various thiols using triethylamine as the catalyst.

The influence of halogen group type on the reactivity of thiol-halogen reaction was investigated in detail by treating the copolymers containing different halogen groups (Table 1, entries B1-3) with methyl mercaptoacetate for 3 h at 50 °C (Table 2, entries 1-3). As illustrated by the $^1$H NMR spectra of the products (Fig. S1), the functionalization degrees are 100%, 25% and 0 for the propylene/IUD, propylene/BrUD and propylene/ClUD copolymers, respectively. Therefore, 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. The analytic details are shown in Supporting Information (SI).

Polymer Chemistry Accepted Manuscript

**Table 2** The syntheses of functional polypropylenes via thiol-halogen reaction[a]

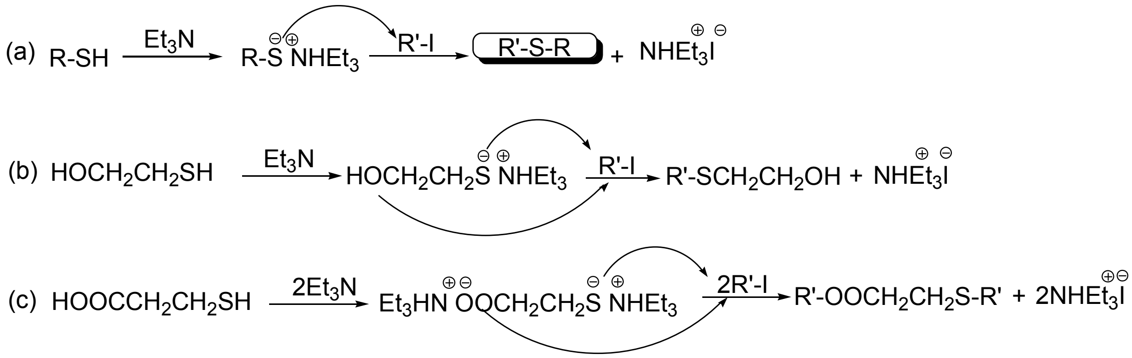
| Entry | Thiol | Comon.[b] (mol%) | Time[c] (h) | Degree[d] (%) |
|---|---|---|---|---|
| 1 | $HSCH_2COOCH_3$ | IUD (7.38) | 3.0 | >99 |
| 2 | $HSCH_2COOCH_3$ | BrUD (7.20) | 3.0 | 25 |
| 3 | $HSCH_2COOCH_3$ | ClUD (7.11) | 3.0 | 0 |
| 4 | $HSCH_2CH_2COOCH_3$ | IUD (7.38) | 3.0 | 39 |
| 5 | $HSCH_2CH_2OH$ | IUD (7.38) | 3.0 | 20 |
| 6 | $HSCH_2CH_2CH_3$ | IUD (7.38) | 3.0 | 13 |
| 7 | $HSCH_2CH(OH)CH_2OH$ | IUD (7.38) | 3.0 | 11 |
| 8 | $HSCH_2COOCH_3$ | IUD (7.06) | 3.0 | >99 |
| 9 | $HSCH_2CH_2COOCH_3$ | IUD (7.06) | 8.0 | >99 |
| 10 | $HSCH_2CH_2OH$ | IUD (7.06) | 15 | >99 |
| 11 | $HSCH_2CH(OH)CH_2OH$ | IUD (7.06) | 24 | >99 |
| 12 | $HSC_6H_5$ | IUD (7.06) | 2.0 | >99 |
| 13 | $HSC_6H_4NH_2$ | IUD (7.06) | 2.5 | >99 |
| 14 | $HSC_6H_4NCS$ | IUD (7.06) | 1.5 | >99 |

[a] Conditions: 50 mg copolymer obtained by *rac*-Et(Ind)$_2$ZrCl$_2$ for entries 1-7, 50 mg copolymer obtained by dimethyl (pyridyl-amido)hafnium for entries 8-14, thiol (100 eq. of halogen groups), triethylamine (100 eq. of halogen groups), 10 mL decalin, 5 mL DMF, T = 50 °C. [b] Copolymers with different incorporations of comonomers. [c] Reaction time. [d] Degrees of functionalizations (%) established by $^1$H NMR spectra.

Just as the copolymers containing different halogens exhibit varied propensities towards methyl mercaptoacetate, not all the thiols are equally reactive. In order to illuminate the influence of thiol structure on reactivity, propylene/IUD copolymer produced by Cat. Zr (Table 1, entry B3) was chosen to react with different thiols, including $HSCH_2COOCH_3$, $HSCH_2CH_2CH_3$, $HSCH_2CH_2COOCH_3$, $HSCH_2CH(OH)CH_2OH$ and $HSCH_2CH_2OH$. In the presence of $Et_3N$, the thiol-halogen reactions at 50 °C were tracked for 3 h by $^1$H NMR spectra. The experimental data are summarized in Table 2 and $^1$H NMR spectra of resulting functionalized products are given in Fig. S1. After treating the copolymer with $HSCH_2COOCH_3$ (Table 2, entry 1), the resonances attributed to -C*H*$_2$I disappeared completely and new peaks corresponding to functional groups appeared in the $^1$H NMR spectrum. Under the same reaction conditions, in the case of $HSCH_2CH_2COOCH_3$ and

Polymer Chemistry Accepted Manuscript

$HSCH_2CH_2CH_3$ functionalized polypropylenes, most of the peaks attributed to -$CH_2I$ still remained in the $^1H$ NMR spectra and the functionalization degrees are about 39 % and 13 %, respectively (Table 2, entries 4, 6). Thus, the reactivity increases following the order: $HSCH_2CH_2CH_3$ < $HSCH_2COOCH_3$ < $HSCH_2CH_2COOCH_3$.



**Scheme 2** The proposed mechanism for thiol-halogen nucleophilic substitution click chemistry.

The acidity of -SH, which is influenced by electron-withdrawing inductive effect of the group adjacent to the sulfydryl, is responsible for such diverse reactivity. As illustrated in Scheme 2a, the generation of quaternary ammonium salt *via* the reaction of mercaptan with triethylamine plays an important role in thiol-halogen reaction. Firstly, the reaction is initiated via acid-base reactions resulting in the formation of quaternary ammonium salt. Secondly, thiol functionalized polypropylene yields via the $S_N2$ nucleophilic addition reaction of thiol anion to R’-I. High acidity of sulfydryl is beneficial for the generation of ammonium salt, thus leading to enhanced reactivity in thiol-halogen reaction. Electron-withdrawing inductive effect of neighboring group in thiol, which can be enhanced by increasing the electron-withdrawing ability of neighboring group and reducing the distance between the group and -SH, is propitious to improve the acidity of thiol. As shown in the $^1H$ NMR spectra of functional polypropylenes (Fig. S1), the chemical shift values of the methylene protons adjacent to the sulfur atom are 2.59 ppm for -S$CH_2CH_2CH_3$, 2.66 ppm for -S$CH_2CH_2COOCH_3$, and 3.33 ppm for -S$CH_2COOCH_3$, respectively. In general, the chemical shift moves to low field with increasing the electron-withdrawing inductive effect. Therefore, the electron-withdrawing inductive effect of neighboring group in thoil undoubtedly has the sequence

Polymer Chemistry Accepted Manuscript

of $HSCH_2COOCH_3$ > $HSCH_2CH_2COOCH_3$ > $HSCH_2CH_2CH_3$. Consequently, the reactivity of thiols was shown as $HSCH_2COOCH_3$ > $HSCH_2CH_2COOCH_3$ > $HSCH_2CH_2CH_3$. However, in spite of the stronger electron-withdrawing inductive effect of hydroxyl than alkyl, as for the 1-thioglycerol and 2-mercaptoethanol functionalized polypropylene, the degrees of the functionalizations are only about 11% and 20%, respectively, while the degree of 1-propanethiol functionalization is 13%, under the same conditions (Table 2, entries 5-7). The reason might be that -OH attempts to compete with -SH to participate in the $S_N2$ nucleophilic addition reaction (Scheme 2b), which retards the nucleophilic addition reaction of thiol anion to R'-I. In conclusion, the sequence of the reactivity for different thiols depends on not only the acidity of the sulfydryl but also the competition of the polar group in the thiols with -SH to participate in the nucleophilic substitution reaction. Particularly noteworthy was our observation that the thiol functionality of $HSCH_2COOCH_3$, $HSCH_2CH_2COOCH_3$, $HSCH_2CH(OH)CH_2OH$ and $HSCH_2CH_2OH$ exclusively added to pendant halogen functionalized polymers, due to the relatively high nucleophilicity of sulfydryl compared to alcohol and ester. In addition, the thiol displacement was also favored in systems containing aliphatic amines. While, crosslinking of the copolymer was detected when $HSCH_2COOH$ was used in the reaction, which was evidenced by the fact that the functionalized polymer could not be completely dissolved in *o*-$C_6D_4Cl_2$ at 125 °C but the new bonds at 1050 $cm^{-1}$ (C-S) and 1750 $cm^{-1}$ (C=O) appeared in the FT-IR spectrum of the product (Fig. S2). This result might be ascribed to the carboxyl anion, stemming from the reaction of carboxylic acid with triethylamine. Such an anion has relatively high nucleophilicity and thus can also substitute the pendant iodine group (Scheme 2c).

### The preparation of various side-group functionalized polypropylenes

Based on the above analysis, subsequently, the propylene/IUD copolymers with high molecular weights (> 100 kg/mol) and high isotacticity ([mmmm] > 99%) as well as highly reactive pendent C-I bond produced by Cat. Hf (IUD content = 7.06 mol%, Table 1, entry A2) were reacted with different thiols, including mercaptoethanol, 1-thioglycerol, methyl mercaptoacetate, methyl mercaptopropionate, 2-mercaptoethylamine, mercaptoacetic acid, thiophenol, 2-aminothiophnol and

Polymer Chemistry Accepted Manuscript

2-mercaptobenzothiazole. After a certain period of time, all of the $HSCH_2COOCH_3$, $HSCH_2CH_2COOCH_3$, $HSCH_2CH(OH)CH_2OH$ and $HSCH_2CH_2OH$ functionalized reactions proceed in a quantitative way (Table 2, entries 8-11). The signals of typical functional copolymers in $^1H$ NMR spectra (Fig. 1) are assigned according to the previous literature.[50] As shown in Fig. 1, the peak corresponding to the -$CH_2$I, originally at 3.20 ppm, is absent in the $^1H$ NMR spectra of the functionalized products. The appearance of peaks at 3.72 and 3.70 ppm (Fig. 1b and 1c) is ascribed to methoxy in ester group, suggesting that the methyl mercaptoacetate and methyl mercaptopropionate functionalized *i*PPs are successfully synthesized. New peaks at 3.79, 2.91-2.48 ppm can be clearly observed in the $^1H$ NMR spectrum of the functionalized product by mercaptoethanol (Fig. 1d), which are ascribed to the methylene protons adjacent to the hydroxyl and the sulfur atom, respectively. For 1-thioglycerol functionalized polypropylene, the characteristic peaks corresponding to methylene and methine protons adjacent to the two hydroxyl groups appear at 3.58-4.00 ppm after the thiol-halogen reaction (Fig. 1e). In FT-IR spectra, the appearance of new absorptions at 3360 $cm^{-1}$ (-OH), 1054 $cm^{-1}$ (C-S) (Fig. 2(4)) and 3400 $cm^{-1}$ (-OH), 1051 $cm^{-1}$ (C-S) (Fig. 2(5)) indicates the successful synthesis of mercaptoethanol and 1-thioglycerol functionalized *i*PPs, respectively. The successful methyl mercaptoacetate and methyl mercaptopropionate functionalizations are further confirmed by the appearance of new absorptions at 1750 $cm^{-1}$ (C=O), 1056 $cm^{-1}$ (C-S) (Fig. 2(2)) and 1735 $cm^{-1}$ (C=O), 1050 $cm^{-1}$ (C-S) (Fig. 2(3)), respectively.

Generally, the acidity of sulfydryl in thiophenol is far higher than that of sulfydryl in alkyl mercaptan because of the electron-withdrawing inductive effect of benzene ring. Based on the above research, we speculated that thiophenol derivatives would exhibit higher reactivity in the thiol-halogen reactions than the corresponding derivatives of alkyl mercaptan. The hypothesis was confirmed by the experimental results. The conversion could reach completion within 2 h in the thiol-halogen reaction employing thiophenol, while the functionalization degree was only 13 % in 3 h when propylmercaptan was used. In order to introduce amino group into polypropylene, which is important but challenging in the field of polyolefin,[51] we carried out the thiol-halogen click chemistry of reactive polypropylene with 2-mercaptoethylamine. However, the $-NH_2$ might participate in the reaction, and cross-linked polymer was obtained, due to the lower reactivity of the -SH. In our following work, we substituted 2-aminothiophenol for 2-mercaptoethylamine and

Polymer Chemistry Accepted Manuscript

successfully introduced amino group into polypropylene with high efficiency. The conversion reached nearly 100% within 2.5 hours and the products with well-defined structures were completely soluble in common organic solvents at elevated temperature. This result can be explained as that the activity of -SH in thiophenol derivatives is high enough to suppress the reactive amino group to interact with the iodinated chain. 2-Mercaptobenzothiazole with high acidity also exhibited high activity in the reaction and the conversion reached completion within 1.5 h.

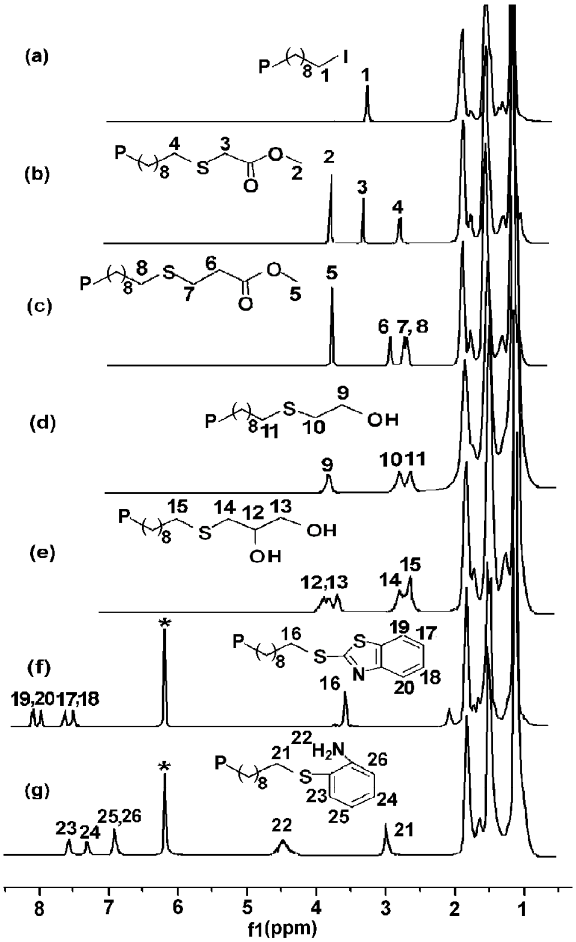


**Fig. 1** $^1$H NMR spectra ($o$-$C_6D_4Cl_2$, 125 °C) for: (a) propylene/IUD copolymer; (b) methyl mercaptoacetate functionalized *i*PP; (c) methyl mercaptopropionate functionalized *i*PP; (d) mercaptoethanol functionalized *i*PP; (e) 1-thioglycerol functionalized *i*PP. $^1$H NMR spectra ($C_2D_4Cl_2$, 125 °C) for: (f) 2-aminothiophnol functionalized *i*PP; (g) 2-mercaptobenzothiazole functionalized *i*PP. All the functional polymers are originated from poly(propylene-*co*-IUD)s produced by Cat. Hf (IUD mol% = 7.06 %, Table 1, entry A2). “P” refers to polymer chain.

Polymer Chemistry Accepted Manuscript

The successful functionalizations of 2-mercaptobenzothiazole and 2-amino thiophenol are illustrated by the $^1$H NMR spectra (Fig. 1f, g). The peaks at 3.20 ppm corresponding to the -$CH_2$I are absent in the spectra of the products. New resonances at 3.00, 6.80-7.66 ppm and 3.55, 7.40-8.14 ppm, which are ascribed to the methylene protons adjacent to the sulfur atom and the aromatic protons, respectively, can be clearly detected. In FT-IR spectra, the appearance of new absorptions at 1714 cm$^{-1}$ (N=C), 1050 cm$^{-1}$ (C-S) (Fig. 2(6)) and 3252-3560 cm$^{-1}$ (-$NH_2$), 1054 cm$^{-1}$ (C-S) (Fig. 2(7)) further confirmed the successful syntheses of 2-amino thiophenol and 2-mercaptobenzothiazole functionalized polypropylenes.

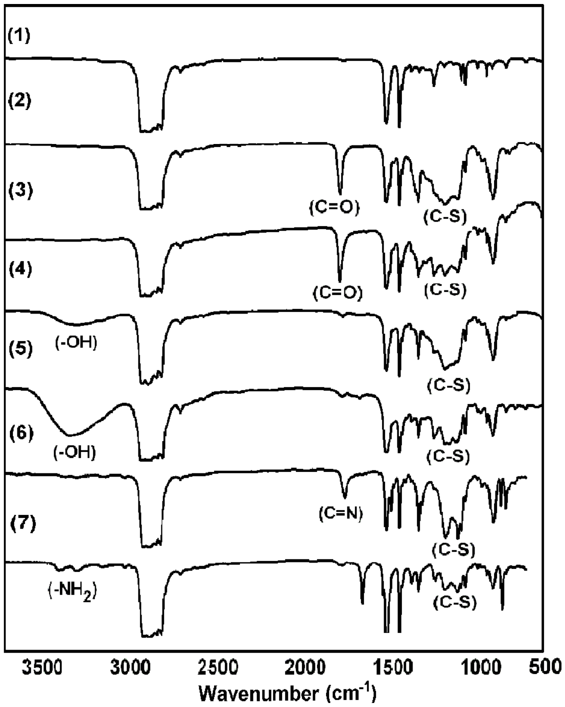


**Fig. 2** FT-IR spectra for: (1) propylene/IUD copolymer; (2) methyl mercaptoacetate functionalized *i*PP; (3) methyl mercaptopropionate functionalized *i*PP; (4) mercaptoethanol functionalized *i*PP; (5) 1-thioglycerol functionalized *i*PP; (6) 2-mercaptobenzothiazole functionalized *i*PP; (7) 2-aminothiophnol functionalized *i*PP; All the functional polymers are originated from poly(propylene-*co*-IUD)s produced by Cat. Hf (IUD mol% = 7.06 %, Table 1, entry A2).

These quantitative functionalizations indicate low occurrence of side reactions during the thiol-halogen reactions. It is important since this strategy not only introduces functional group simply and efficiently but also produces the functional polypropylenes with well-defined structures. Typical GPC curves of the functional copolymers before and after the thiol-halogen reaction are presented in Fig. S3 (see Supporting Information). As observed, after thiol-halogen reaction, the GPC curves of functional polypropylenes have remained more or less unchanged with unimodal

Polymer Chemistry Accepted Manuscript

molecular weight distributions, indicating crosslinking is negligible in these functional reactions. Fig. S4 compares DSC curves of functional copolymers before and after the thiol-halogen click chemistry. Only a single peak with a relatively narrow width is observed throughout the entire composition range in the heating cycles. Obviously, all $T_m$ values decrease with the enhancement of the density of polar comonomer in the functional copolymers. While the transformation of iodine groups to other functional groups has little effect on $T_m$ values. Evidently, the *i*PP crystalline structure is mainly governed by functionalization density.

**The preparation of *i*PP-*g*-PLLA *via* ring-opening graft-copolymerization**

The aliphatic polyesters, such as poly(L-lactide) (PLLA) and poly(ε-caprolactone) (PCL), are semi-crystalline macromolecules. They possess biodegradability and excellent mechanical properties. Thus the introduction of aliphatic polyester graft chain into *i*PP is an ideal strategy to broaden the *i*PP's applications to higher value products. The *i*PP containing hydroxyl group generated from the thiol-halogen reaction could be employed to initiate the ring-opening polymerization (ROP) of cyclic aliphatic ester monomer. We employed the iodinated *i*PP with lower content of IUD units (3.54 mol%) as the reactive intermediates, because high graft density will lose the desired properties of polyolefin backbone. After the thiol-halogen reaction with 2-mercaptoethanol, hydroxylated copolymer could be easily synthesized. Catalyzed by $Sn(Oct)_2$, the obtained hydroxylated *i*PP initiated the ROP of L-lactide at 90 °C. After the Soxhlet extraction with THF for 24 h to remove L-lactide homopolymer, the obtained *i*PP-*g*-PLLA copolymers are fully characterized by $^1$H NMR spectra, IR spectra, and DSC analyses.

The microstructure of the *i*PP-*g*-PLLA copolymer is established by $^1$H NMR (Fig. 3) and all chemical shifts observed can be assigned clearly according to previous literatures [52,53]. The PLLA content was increased from 34.5 wt.% to 69.9 wt.% by only extending the reaction time from 1.0 h to 1.5 h, according to NMR analyses. Proton signals at 2.61, 2.77 and 3.79 ppm attributed to $-CH_2SCH_2CH_2OH$ (marked as "2, 3, 4") completely migrated to 2.65, 2.81 and 4.41 ppm (marked as "5, 6, 7"), indicating the formation of $-CH_2SCH_2CH_2$-PLLA. This confirmed that the *i*PP precursors have been completely converted into graft copolymers. Moreover, in addition to the appearance of peaks corresponding to PP main chain (0.96-1.96 ppm) and PLLA graft chain (5.35 and 1.67 ppm), the characteristic peaks assigned to methyl (1.32 ppm, marked as "11") and methine (3.75 ppm, marked as "10") adjacent to terminated hydroxyl were also observed, further confirming

Polymer Chemistry Accepted Manuscript

the successful initiation of the hydroxylated *i*PP. Besides, the area integral of peak 5 is twice of peak 10, which demonstrates no detectable PLLA homopolymer existed in the samples. The successful ROP can also be validated by FT-IR spectra (Fig. S5) which display new absorption at 1751 cm$^{-1}$ assigned to the stretching vibration of C=O in PLLA graft chain. The thermal transition temperatures of *i*PP-*g*-PLLA copolymers were examined by DSC analysis (typical DSC curves are shown in Fig. 4). The *i*PP-*g*-PLLA copolymer with low PLLA content (34.5 wt%) possesses only one melting temperature ($T_m$) peak around 125 °C corresponding to the $T_m$ of *i*PP main chain. However, the *i*PP-*g*-PLLA copolymer with high PLLA content (69.9 wt%) exhibits two $T_m$ peaks, which indicated that the phases corresponding to the *i*PP backbone ($T_m$ = 124 °C) and PLLA graft chain ($T_m$ = 141 °C) are evidently separated.

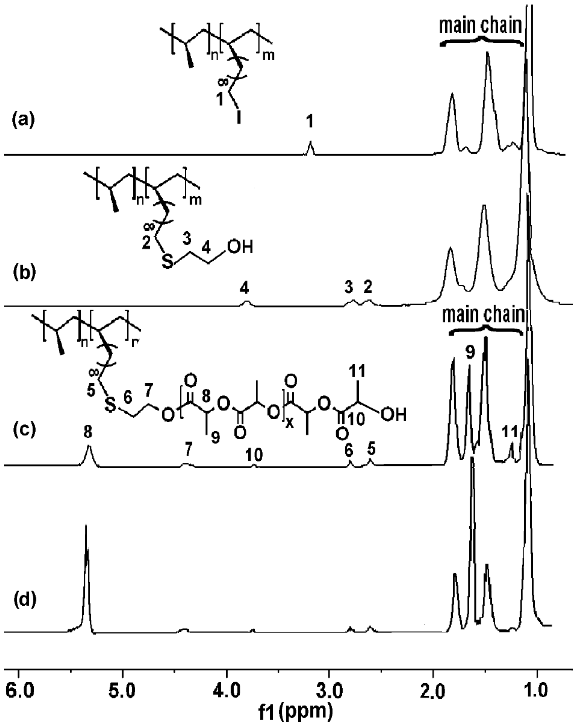


**Fig. 3** $^1$H NMR spectra ($o$-$C_6D_4Cl_2$, 125 °C) for: (a) propylene/IUD copolymer; (b) mercaptoethanol functionalized *i*PP; (c) *i*PP-*g*-PLLA graft copolymers with 34.5 wt.% of LLA units; (d) *i*PP-*g*-PLLA graft copolymers with 69.9 wt.% of LLA units. All the functional polymers are originated from poly(propylene-*co*-IUD)s produced by Cat. Hf (IUD mol% = 3.54%, Table 1, entry A1).

Polymer Chemistry Accepted Manuscript

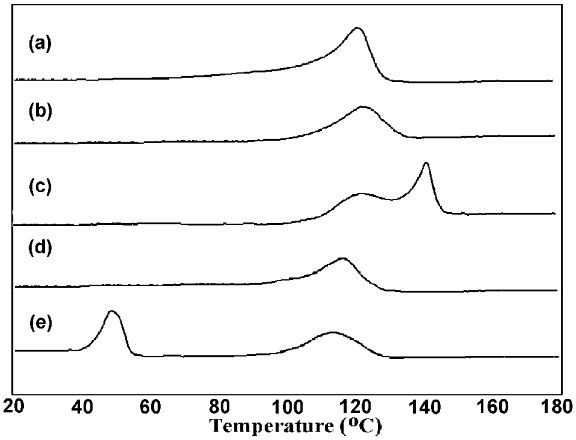


**Fig. 4** The DSC curves (at a rate of 10 °C/min) for: (a) $T_m$=124 °C (propylene/IUD copolymer, IUD mol% = 3.53%, Table 1, entry A1); (b) $T_m$ = 125 °C (*i*PP-*g*-PLLA graft copolymers with 34.5 wt.% of LLA units); (c) $T_{m1}$ = 124 °C, $T_{m2}$ = 141 °C (*i*PP-*g*-PLLA graft copolymers with 69.9 wt.% of LLA units); (d) $T_m$ = 122 °C (*i*PP-*g*-PCL graft copolymers with 38.6 wt.% of CL units); (e) $T_{m1}$ = 50 °C, $T_{m2}$ = 121 °C (*i*PP-*g*-PCL graft copolymers with 71.7 wt.% of CL units).

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

The graft-from approach mentioned above can be used to prepare graft functionalized *i*PPs with high efficiency, whereas the length of the graft chain cannot be easily controlled. The copolymer containing iodine group can be directly utilized in click coupling reaction with sulfydryl end functionalized aliphatic polyesters, providing functional graft polypropylene copolymer with defined graft chain length *via* graft-onto approach. Different from previous reported functionalization of polyolefins *via* click coupling reaction, this strategy has a remarkable advantage in direct and convenient synthesis without requiring functional group transformation.[54-58] Initiated by 2-mercaptoethanol, poly(ε-caprolactone) (PCL-RSH, $M_n$ = 1,070 g/mol with PDI = 1.2) was conveniently and directly synthesized *via* the ROP of ε-caprolactone using immobilized lipase Novozym 435 as a chemoselective catalyst, saving tedious protecting and deprotecting steps.[59,60] Likewise, the polypropylene intermediate with lower IUD content (3.54 mol%) was used in the following click coupling reaction to maintain the excellent physical properties of PP main chain in the graft products. The coupling reaction run at 70 °C for 24 h, and the collected product mass were socked in and washed with dichloromethane for more than five times to remove unreacted

Polymer Chemistry Accepted Manuscript

PCL-RSH. The $^1$H NMR spectrum (Fig. 5b) indicated that the most peaks attributed to -C$H_2$I still remained in the spectrum, and only small part of the iodinated polypropylene was transformed into the functionalized product which displayed the characteristic peak at 2.64 ppm corresponding to the formed -$CH_2$SCH$_2$CH$_2$-PCL protons (marked as "2"). The degree of conversion is only about 25%, mainly due to the "polymer effect", the low reactivity of the -SH adjacent to alkyls and the competition of -OH located on the other end of the polymer chain.

The systematic investigation about the thiol-halogen click chemistry mentioned above suggested that the activity of thiophenol was far higher than that of alkyl mercaptan. Inspired by this conclusion, in order to improve the reactivity of -SH end group, we employed (2-mercaptophenyl)methanol instead of 2-mercaptoethanol as the initiator in the ROP of ε-caprolactone to produce thiophenol terminated poly(ε-caprolactone) (PCL-PhSH). The coupling reactions between PCL-PhSH and propylene/IUD copolymer were performed at 70 °C for 24 h. By employing PCL-PhSHs with different $M_n$s ($M_n$ = 1,100 or 2,070 g/mol with PDI $\leq$ 1.2), the graft copolymers with defined graft length have been prepared and the PCL content can be tuned from 38.6 to 71.7 wt%. The signals of typical graft copolymers in $^1$H NMR spectra (Fig. 5) were assigned according to the ref. 53 and 61. As shown in Fig. 5c, the proton signals corresponding to -C$H_2$I- at 3.20 ppm (marked as "1" in 5a) disappeared completely after the click coupling reaction, while the new proton signals at 3.09 ppm attributed to -C$H_2$S- were detected (marked as "10"), indicative of a full conversion of the iodine groups to PCL graft chains. In addition to the appearance of peaks corresponding to PP main chain (0.88-1.98 ppm) and PCL graft chain (2.50, 4.27 ppm, marked as "13, 14"), the characteristic peaks at 3.82 and 5.46 ppm, respectively, assigned to methylene adjacent to the terminated hydroxyl and the aromatic ring (marked as "11, 12") could also be observed. Besides, the integral of peak 10 is equivalent to that of peak 11, confirming that the samples are homogeneous graft copolymers and no detectable homopolymer PCL-PhSH existed. The successful click coupling reaction was further confirmed by FT-IR spectra (Fig. S5) which displayed new absorption at 1722 cm$^{-1}$ assigned to the stretching vibration of C=O in PCL graft

Polymer Chemistry Accepted Manuscript

chain. The thermal transition temperatures of graft copolymers were examined by DSC analysis. As observed, *i*PP-*g*-PCL copolymer with high PCL content (71.7 wt.%) has two melting temperatures (Fig. 4e). The high temperature peak at about 121 °C is attributed to the $T_m$ of PP main chain and the low one at about 50 °C is assigned to the $T_m$ of PCL graft chain. The $T_m$ value corresponding to PCL graft chain is lower than that attributed to the homopolymer PCL-PhSH in the poly(propylene-*co*-IUD)/PCL-PhSH blends (Fig. S7), might because that the *i*PP main chain retards the crystallization of the PCL graft chain in the graft copolymer. This further confirms the homogeneous composition of the graft copolymers. In contrast, *i*PP-*g*-PCL copolymer with low PCL content (38.6 wt%) only exhibits one melting temperature attributed to PP segments in the main chain, while the melting temperature of PCL graft chain is indistinct probably because of the lower crystallization of the low molecular weight PCL (Fig. 4d). These results demonstrate that the graft functionalized *i*PPs could be conveniently and efficiently achieved *via* graft-onto or graft-from approach based on the thiol-halogen click chemistry.

Moreover, both the graft-onto and graft-from reactions were monitored by GPC (with light scattering detector) and typical curves are exhibited in Fig. S8. As observed, for each kind of graft copolymers (*i*PP-g-PCL or *i*PP-g-PLLA), the molecular weights increased with the content of the ester units and the unimodal distributions retained. These results further confirmed that the graft copolymers rather than homopolymer blends have been obtained. However, the real molecular weight of the graft copolymers should be higher than those from GPC, considering that thermal degradation might occurred during the processes of dissolution and measurement at high temperature above 150 °C.[62,63]

Polymer Chemistry Accepted Manuscript

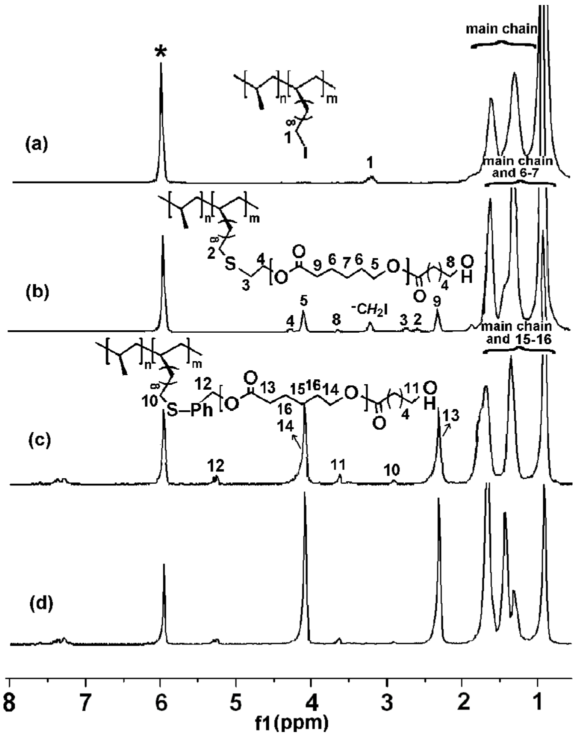


**Fig. 5** $^1$H NMR spectra ($C_2D_4Cl_2$, 125 °C) for: (a) propylene/IUD copolymer; (b) *i*PP-*g*-PCL graft copolymers derived from the coupling between propylene/IUD copolymer and PCL-RSH; (c) *i*PP-*g*-PCL graft copolymers derived from the coupling between propylene/IUD copolymer and PCL-PhSH with 38.6 wt.% of CL units; (d) *i*PP-*g*-PCL graft copolymers derived from the coupling between propylene/IUD copolymer and PCL-PhSH with 71.7 wt.% of CL units. All the functional polymers are originated from poly(propylene-*co*-IUD)s produced by the Cat. Hf (IUD mol% = 3.54%, Table 1, entry A1).

## Conclusion

To better take advantage of thiol-halogen click chemistry to develop diverse functional *i*PP materials, the influence factors on the reactivity of the thiol-halogen reaction involving halogenated *i*PP have been systematically investigated for the first time. The order of copolymers reactivity can be summarized as iodinated >> brominated > chlorinated *i*PP, while for different thiols, the reactivity depends on not only the acidity of the sulfydryl but also the competition of the polar group with -SH to participate in the nucleophilic substitution reaction. Based on this, the thiol-halogen reactions between poly(propylene-*co*-ω-iodo-α-undecene) and different thiols were conducted and provided functional *i*PPs containing various groups, including hydroxyl, ester, aryl, thiazolyl and amino, in a quantitative way. The functional products possess high molecular weights

Polymer Chemistry Accepted Manuscript

($M_w$ > 100 kg/mol) and high isotacticity ([mmmm] > 99%) with the content of polar group tuned in a wide range of 0-11 mol%. Furthermore, this investigation inspired the convenient introduction of the reactive amino into polyolefin and the preparation of poly(ε-caprolactone)s with highly reactive -SH end (PCL-PhSH) *via* enzyme-assisted ring-opening polymerization. The hydroxylated *i*PP generated from the functionalization with 2-mercaptoethanol could initiate the ring-opening polymerization of L-lactide, resulting in functional polypropylene graft copolymers (*i*PP-*g*-PLLA) with high efficiency. The retained iodine group in propylene/IUD copolymer can be directly utilized in click coupling reactions with PCL containing highly reactive -SH end (PCL-PhSH) and well-defined functional polypropylene graft copolymers (*i*PP-*g*-PCL) with tunable PCL contents were successfully synthesized.

## Supporting Information

The detailed experimental procedures; $^1$H NMR spectra for the systematic investigation of the influence factors (halogen type and thiol structure) on the reactivity of thiol-halogen reaction; FT-IR spectra for mercaptoacetic acid functionalized polypropylene; typical DSC and GPC profiles for functional polypropylenes before and after thiol-halogen reaction; FT-IR spectra for graft copolymers; $^1$H and $^{13}$C NMR spectra of PCL-PhSH.

## Acknowledgements

The authors are grateful for subsidy provided by the National Natural Science Foundation of China (No. 21234006).

## References

1 P. Galli and G. Vecellio, *Prog. Polym. Sci.*, 2001, **26**, 1287-1336.
2 N. K. Boaen and M. A. Hillmyer, *Chem. Soc. Rev.*, 2005, **34**, 267-275.
3 A. Nakamura, S. Ito and K. Nozaki, *Chem. Rev.*, 2009, **109**, 5215-5244.
4 H. Hagihara, K. Tsuchihara, J. Sugiyama, K. Takeuchi and T. Shiono, *Macromolecules*, 2004, **37**, 5145-5148.
5 S. Coiai, E. Passaglia, M. Aglietto and F. Ciardelli, *Macromolecules*, 2004, **37**, 8414-8423.
6 C. Bae, J. F. Hartwig, N. K. Boaen Harris, R. O. Long, K. S. Anderson and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2005, **127**, 767-776.

Polymer Chemistry Accepted Manuscript

7 K. Wakabayashi, C. Pierre, D. A. Dikin, R. S. Ruoff, T. Ramanathan, L. C. Brinson and J. M. Torkelson, *Macromolecules*, 2008, **41**, 1905-1908.

8 T. C. Chung, *Macromolecules*, 2010, **43**, 7482-7487.

9 M. Kobayashi, T. Matsugi, J. Saito, J. Imuta, N. Kashiwa and A. Takahara, *Polym. Chem.*, 2013, **4**, 731-739.

10 M. R. Kesti, G. W. Coates and R. M. Waymouth, *J. Am. Chem. Soc.*, 1992, **114**, 9679-9680.

11 U. M. Stehling, K. M. Stein, M. R. Kesti and R. M. Waymouth, *Macromolecules*, 1999, **32**, 14-20.

12 M. J. Schneider, R. Schäfer and R. Mülhaupt, *Polymer*, 1997, **38**, 2455-2459.

13 L. S. Boffa and B. M. Novak, *Chem. Rev.*, 2000, **100**, 1479-1494.

14 S. D. Ittel, L. K. Johnson and M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169-1203.

15 G. H. Chen, X. S. Ma and Z. B. Guan, *J. Am. Chem. Soc.*, 2003, **125**, 6697-6704.

16 E. Drent, R. Dijk, R. Ginkel, B. Oort and R. I. Pugh, *Chem. Commun.*, 2002, 744-745.

17 S. Luo, J. Vela, G. R. Lief and R. F. Jordan, *J. Am. Chem. Soc.*, 2007, **129**, 8946-8947.

18 T. Runzi, D. Frohlich and S. Mecking, *J. Am. Chem. Soc.*, 2010, **132**, 17690-17691.

19 S. Ito, M. Kanazawa, K. Munakata, J. I. Kuroda, Y. Okumura and K. Nozaki, *J. Am. Chem. Soc.*, 2011, **133**, 1232-1235.

20 R. P. Singh, *Prog. Polym. Sci.*, 1992, **17**, 251-281.

21 J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Jr. Harris, E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton and S. H. Phillips, *Chem. Mater.*, 2000, **12**, 1866-1873.

22 P. Maiti, P. H. Nam, M. Okamoto, N. Hasegawa and A. Usuki, *Macromolecules*, 2002, **35**, 2042.

23 S. S. Ray and M. Okamato, *Prog. Polym. Sci.*, 2003, **28**, 1539-1641.

24 O. Foster, A. H. Soeriyadi, M. R. Whittaker, T. P. Davis and C. Boyer, *Polym. Chem.*, 2012, **3**, 2102-2111.

25 T. C. Chung and D. Rhubright, *Macromolecules*, 1993, **26**, 3019-3025.

26 J. Y. Dong, E. Manias and T. C. Chung, *Macromolecules*, 2002, **35**, 3439-3447.

27 T. C. Chung and H. L. Lu, *J. Polym. Sci., Polym. Chem. Ed.*, 1997, **35**, 575-579.

28 T. C. Chung and H. L. Lu, *J. Polym. Sci., Polym. Chem. Ed.*, 1999, **37**, 2795-2802.

29 T. C. Chung, S. Hong and H. L. Lu, *Macromolecules*, 1998, **31**, 2028-2034.

30 B. Lu and T. C. Chung, *J. Polym. Sci., Polym. Chem. Ed.*, 2000, **38**, 1337-1343.

31 M. Zhang, R. H. Colby, S. T. Milner and T. C. Chung, *Macromolecules*, 2013, **46**, 4313-4319.

32 J. Y. Dong and T. C. Chung, *Macromolecules*, 2002, **35**, 2868-2870.

33 J. Y. Dong, H. Hong, T. C. Chung, H. C. Wang and S. Datta, *Macromolecules*, 2003, **36**, 6000-6009.

Polymer Chemistry Accepted Manuscript

34 W. Lin, Z. Shao, J. Y. Dong and T. C. Chung, *Macromolecules*, 2009, **42**, 3750-3754.

35 N. Kawahara, J. Saito, S. Matsuo, H. Kaneko, T. Matsugi, S. Kojoh and N. Kashiwa, *Polym. Bull.*, 2007, **59**, 177-183.

36 S. Bruzaud, H. Cramail, L. Duvignac and A. Deffieux, *Macromol. Chem. Phys.*, 1997, **198**, 291-303.

37 R. Bacskai, *J. Polym. Sci.*, *Part A*, 1965, **3**, 2491-2510.

38 K. J. Zhang, Z. B. Ye and R. Subramanian, *Macromolecules*, 2008, **41***,* 640-649.

39 K. J. Zhang, J. L. Wang, R. Subramanian, Z. B. Ye, J. M. Lu and Q. Yu, *Macromol. Rapid Commun.*, 2007, **28**, 2185-2191.

40 J. Mazzolini, E. Espinosa, F. D'Agosto and C. Boisson, *Polym. Chem.*, 2010, **1**, 793-800.

41 R. Godoy, F. D'Agosto and C. Boisson, *Prog. Polym. Sci.*, 2007, **32**, 419-454.

42 S. Y. Li and Z. B. Ye, *Macromol. Chem. Phys.*, 2010, **211**, 1917-1924.

43 C. E. Hoyle, A. B. Lowe and C. N. Bowman, *Chem. Soc. Rev.*, 2010, **39**, 1355-1387.

44 B. M. Rosen, G. Lligadas, C. Hahn and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 3940-3948.

45 D. Samaroo, M. Vinodu, X. Chen and C. M. Drain, *J. Comb.Chem.*, 2007, **9**, 998-1011.

46 C. R. Becer, K. Babiuch, D. Pilz, S. Hornig, T. Heinze, M. Gottschaldt and U. S. Schubert, *Macromolecules*, 2009, **42**, 2387-2394.

47 S. Martínez-Arranz, A. C. Albéniz and P. Espinet, *Macromolecules*, 2010, **43**, 7482-7488.

48 X. Y. Wang, Y. X. Wang, X. C. Shi, J. Y. Liu, C. L. Chen and Y. S. Li, *Macromolecules*, 2014, **47**, 552-559.

49 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.

50 M. Hong, S. R. Liu, B. X. Li, Y. S. Li, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2499-2506.

51 M. Zhang, X. Yuan, L. Wang and T. C. Chung, *Macromolecules*, 2014, **47**, 571-581.

52 Y. Liu, W. S. Dong, J. Y. Liu and Y. S. Li, *Dalton Trans.*, 2014, **43**, 2244-2251.

53 M. Hong, L. Pan, B. X. Li and Y. S. Li, *Polymer*, 2010, **51**, 3636-3643.

54 T. Li, W. Wang, R. Liu, W. Liang, G. Zhao, Z. Y. Li, Q. Wu and F. M. Zhu, *Macromolecules*, 2009, **42**, 3804-3810.

55 K. Satoh, J. E. Poelma, L. M. Campos, B. Stahla and C. J. Hawker, *Polym. Chem.*, 2012, **3**, 1890-1898.

56 M. A. Tasdelen, *Polym. Chem.*, 2011, **2**, 2133-2145.

Polymer Chemistry Accepted Manuscript

57 R. Briquel, J. Mazzolini, T. L. Bris, O. Boyron, F. Boisson, F. Delolme, F. D'Agosto, C. Boisson and R. Spitz, *Angew. Chem., Int. Ed.*, 2008, **47**, 9311-9313.

58 M. Hong, J. Y. Liu, B. X. Li and Y. S. Li, *Macromolecules*, 2011, **44**, 5659-5665.

59 G. Carrot, J. Hilborn, J. L. Hedrick and M. Trollsås, *Macromolecules*, 1999, **32**, 5171-5173.

60 C. Hedfors, E. Östmark, E. Malmström, K. Hult and M. Martinelle, *Macromolecules*, 2005, **38**, 647-649.

61 H. L. Han, Y. Liu, J. Y. Liu, K. Nomura and Y. S. Li, *Dalton Trans.*, 2013, **42**, 12346-12352.

62 M. Kunioka and Y. Doi, *Macromolecules*, 1990, **23**, 1933-1936.

63 T. C. Chung, *Macromolecules*, 2013, **46**, 6671-6698.

Polymer Chemistry Accepted Manuscript