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Fabrication of long chain branched polypropylene using click chemistry

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Abstract This article presents a new method to produce LCBPP with well-defined structures via Huisgen's 1,3-dipolar cycloaddition of azide and alkyne (click reaction). Azide-terminated isotactic polypropylene (iPP) (iPP-St-N_3) was synthesized via the hydrochlorination and subsequent substitution of the starting styryl-terminated i-PP (i-PP-t-St), which is the product of a metallocene-mediated isospecific propylene polymerization governed by a controlled chain transfer reaction. Alkyne-grafted iPP (iPP-g-$\equiv$) can be produced with high efficiency through one-pot esterification and the subsequent amidation of hydroxyl-functionalized iPP. Detailed analysis of the product by ^{1}H NMR, FTIR, DSC, and GPC reveals a clean and clear formation of LCBPP.

Keywords Long chain branched polypropylene · Functionalization · Click chemistry

Introduction

Isotactic polypropylene (iPP) is a leading and fast growing commodity resin in the world due to its desirable and beneficial physical properties, such as high melting point, high stiffness, resistance to corrosive chemicals, and low specific gravity. However, commercial iPP usually exhibits relatively low melt strength, leading to the absence of general PP materials in thermoforming, extrusion coating, and blow molding. Therefore, considerable efforts were made to improve the melt rheological properties of iPP to expand applications of this low cost material. Since long chain branching (LCB) is an ideal technique to improve iPP's melt strength and

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processibility while keeping other desirable properties, several methods were developed to obtain iPP with LCB structure (LCBPP) [1–3].

Reactive extrusion and electron beam irradiation techniques have been widely used to produce LCBPP, which were based on radical-induced chain scission and recombination mechanism, leading to branched polymers with broadened molecular weight distribution and a complex distribution of structures [1, 4–6]. The copolymerization of propylene with nonconjugated α,ω-diene has also been adopted to introduce LCB structure into iPP chain via copolymerization of propylene with vinyl-functionalized macromonomers, which can be derived from single enchainment of diene monomer [2, 7, 8]. However, the potential double enchainment of diene monomer to produce ring structures can consume pendant vinyl moieties and thus decreases the LCB efficiency. In addition, diene concentration must be carefully controlled to obtain iPP with enough LCBs to improve its melt strength, while at the same time avoiding the formation of a cross-linked network. Other approaches utilize in-reactor metallocene copolymerization of propylene with in situ generated (from controlled chain transfer reaction) or externally added macromonomers [3, 9–12], which require delicate selection of reaction conditions to produce vinyl-functionalized macromonomers for copolymerization, and are not able to get pure LCBPP due to the low insertion efficiency of macromonomers.

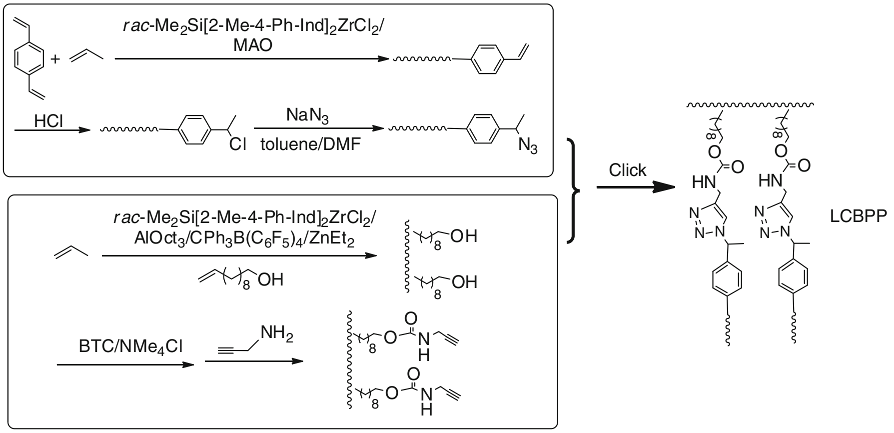
In recent years, one of the most significant research progresses achieved in polymer chemistry is the introduction of click chemistry into polymer science as a highly efficient coupling method to create novel polymer structures [13, 14]. Although not limited to, the most popular click reaction resides on azide-alkyne 1,3-dipolar cycloaddition catalyzed by copper(I) which is advantaged by mild reaction conditions, functional group tolerance and quantitative yields and, as a coupling method, allows the fast and simple creation, from preformed polymer structures, of well-defined and complex polymer structures that were previously unattainable [15–17]. Nowadays, the use of azide-alkyne click chemistry in polymer science has been one of the most rapidly growing fields of research, and a variety of polymer architectures, including end-functionalized polymers, block copolymers, cyclic polymers, graft copolymers, star-shaped copolymers, dendrimers, and crosslinked materials, have been realized by exploiting click chemistry [18–20].

Herein, a new method to prepare LCBPP with well-defined structures was reported. As outlined in Scheme 1, azide-alkyne 1,3-dipolar cycloaddition catalyzed by copper(I) was used to combine backbone and side chain of LCBPP with high efficiency.

Experimental part

Instrumentation and materials

All O_2- and moisture-sensitive manipulations were carried out inside an argon-filled vacuum atmosphere dry-box equipped with a dry train. $CPh_3B(C_6F_5)_4$ (min. 98%, Strem), $AlOct_3$ (Aldrich, 25 wt% in hexane), *N*,*N*-dimethylformamide (DMF,



Scheme 1 Synthetic routes to iPP-St-N_3 and iPP-g-≡ followed by click reaction to produce LCBPP

99.8%, Extra Dry over Molecular Sieve, Acros Organics), sodium azide (NaN_3, Chengdu Kelong Chemical Regents Company of China), diethylzinc ($ZnEt_2$, 1 M solution in hexane, Acros Organics), bis(trichloromethyl)carbonate (BTC, Beijing Ouhe Technology Co. Ltd. of China), NMe_4Cl (98+%, Acros Organics) were used as received. *rac*-$Me_2Si[2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind]_2ZrCl_2$ (SiPh) was prepared according to the procedures described in Ref. [21]. Methylaluminoxane (MAO, 1.4 M in toluene), which was kindly supplied by CNPC Lanzhou Chemical Company, was dried under vacuum to remove trimethylaluminum (TMA), and the resulting TMA free MAO was diluted in toluene before used. Toluene (Sinopharm Chemical Reagent Beijing Co., Ltd. of China) was distilled over sodium and benzophenone under nitrogen before use. CuBr was purified according to a literature procedure [22]. Propargyl amine (Beijing Da Tian Feng Tuo Chemical Technology Co., Ltd. of China) was dried over 4 Å molecular sieve for 2 weeks before use. Pentamethyldiethylenetriamine (PMDETA, 98%, Alfa Aesar), octane, and diethyl ether were refluxed in CaH_2 for at least 48 h before distillation. iPP-St-N_3 was prepared according to a published procedure [23]. Polymerization grade ethylene and propylene were supplied by Yanshan Petrochemical Co. of China.

The melting temperature of the polymers was measured by differential scanning calorimetry (DSC) using a Perkin-Elmer Diamond DSC instrument controller at a heating rate of 10 °C/min. Room temperature ^1H NMR spectra were recorded on a Bruker AVANCE 400 instrument. High temperature ^1H and ^{13}C NMR spectra were carried out at 390 K using a Bruker DMX 300 spectrometer with *o*-dichlorobenzene-d_4 as a solvent. FTIR absorbance data were obtained on a Nicolet 6700 FTIR spectrometer. The molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) using a Waters Alliance GPC 2000 instrument equipped with a refractive index (RI) detector and a set of u-Styragel HT columns of 10^6, 10^5,10^4, and 10^3 pore size in series. The measurement was performed at 150 °C with 1,2,4-trichlorobenzene as the eluent at a flow rate of 0.95 mL/min. Narrow-molecular-weight PS samples were used as standards for calibration.

Synthesis of hydroxyl-grafted i-PP (i-PP-g-OH)

In a typical reaction (Table 2, sample iPP-g-OH-3), in a 250-mL glass reactor equipped with a magnetic stirrer and a thermometer was added 100 mL of toluene under atmospheric pressure of propylene with stirring (600 rpm). Following was the injection of $AlOct_3$ in hexane (8 mmol) and U-OH (3.2 mmol) sequentially. After stirring for 5 min, $ZnEt_2$ in hexane (0.2 mmol) was added as a polymer molecular weight regulator. Then a toluene solution of SiPh (8 μmol) was injected into the reactor. The polymerization reaction was initiated by the addition of a toluene solution of $CPh_3B(C_6F_5)_4$ (10 μmol). After 7 min of reaction, the reaction mixture was poured into an excess of acidic ethanol and the polymer was collected by filtration. After washing three times each with 50 mL of ethanol, the polymer was dried at 50 °C for 12 h in a vacuum oven to obtain a fine white powder 1.08 g.

Synthesis of alkyne-grafted i-PP (i-PP-g-≡)

In a typical reaction, 1.00 g of *i*-PP-*g*-OH-3 (0.35 mmol $g\ PP^{-1}$) polymer was suspended in 60 mL of toluene at ambient temperature. The flask was then heated up with stirring until toluene becomes refluxing. After the polymer flakes were no longer visible, the flask was allowed to cool down to 35 °C in air, with steadily stirring. Then 1.1 g (3.5 mmol) BTC in 30 mL THF was added into the flask. This reaction was allowed to proceed for 1 h, after which 38 mg of NMe_4Cl (0.35 mmol) was introduced into the reaction system. The reaction mixture was stirred for 24 h at 35 °C before being vacuum-dried to remove excess phosgene and solvent. The flask was recharged with 60 mL of toluene and 0.72 mL (10 mmol) of propargyl amine. After another 12 h's stirring at 35 °C, finally the reaction mixture was poured into 200 mL of ethanol. The precipitate was filtered out to obtain a white powder, which was dried under vacuum at 50 °C for 12 h to give 0.89 g *i*-PP-*g*-≡ (89%).

Synthesis of LCB-i-PP via click reaction

An oven-dried round-bottomed flask (25 mL) equipped with a magnetic stirrer and condenser was charged with 85 mg of *i*PP-*g*-≡ (16.2 μmol), 160 mg of *i*PP-St-N_3 (14.4 μmol) (a little excess of iPP-g-≡ was introduced to ensure the complete transformation of iPP-St-N_3 to produce pure LCBPP), 2.9 mg of CuBr (2.1 mg), 15 mL toluene and 5 mL DMF. The mixture was stirred for 1 h at 110 °C. 3 μl PMDETA was then added to initiate the reaction. After 10 h at 120 °C, the reaction mixture was poured into acidified ethanol and the precipitated polymer was purified by repeatedly washing with water and acidified ethanol and finally dried under vacuum at 50 °C for 12 h to give 190 mg of product, yield 78%.

Results and discussion

Synthesis of azide-terminated iPP (iPP-St-N_3)

iPP-St-N_3 was synthesized via a same procedure developed in our group before, through the hydrochlorination and subsequent substitution by sodium azide (NaN_3), of the starting styryl-terminated i-PP (i-PP-t-St), which is the product of a metallocene-mediated isospecific propylene polymerization governed by a controlled chain transfer reaction [23].

Synthesis of alkynyl-grafted iPP (iPP-g-$\equiv$)

Until now, the most frequently used procedure to produce alkyne-terminated polymer is a carbodiimide-mediated coupling reaction of 4-pentynoic acid with hydroxyl-functionalized polymer, and this process has gained great success with those polymers soluble at room temperature [18, 24]. However, this reaction is usually conducted at 0 °C, and the byproduct needs to be filtered off to obtain pure product. All these conditions are unprofitable for a macromolecular reaction involved iPP, which is insoluble in any solvent at room temperature or below. The combination of NaH and propargyl bromide procedure was also used to introduce alkynyl into a small organic molecular at room temperature or below to carry out the next click reaction [25, 26] which is also improper for iPP due to the heterogeneous medium. Esterification of –OH with phosgene and the subsequent amidation by propargyl amine [27–29] is another procedure to introduce aklynyl group into a polymer chain, although it was rarely utilized due to the use of highly toxic phosgene. This process can be operated at room temperature with high efficiency; hence we decided to adopt this route for the synthesis of iPP-g-$\equiv$.

Nowadays, phosgene has been replaced by bis(trichloromethyl) carbonate (BTC) for the most synthetic applications in an ordinary organic laboratory [30–32], which is a safe phosgene source with low toxicity and can be bought conveniently at most regent companies. Therefore, we checked the possibility to use BTC in place of phosgene to transform iPP-g-OH to iPP-g-$\equiv$ and finally found an optimized condition successfully, which is the first report on the production of alkyne-functionalized polyolefin.

Hydroxyl-grafted iPP (iPP-g-OH) was synthesized by simple copolymerization of undecylenyl alcohol (U-OH) with propylene in the presence of $ZnEt_2$ as a chain transfer agent to control the molecular weight of copolymers. Three typical samples were obtained and their characterization data are listed in Table 1.

Table 1 Characterization data iPP-g-OH samples

Sample	$M_n/10^4$	$M_w/10^4$	PDI	c_{OH}/mmol gPP^{-1a}
iPP-g-OH-1	1.19	3.65	3.07	0.14
iPP-g-OH-2	2.06	3.90	1.89	0.35
iPP-g-OH-3	8.19	28.78	3.51	0.19

[a] Determined by ^{1}H NMR

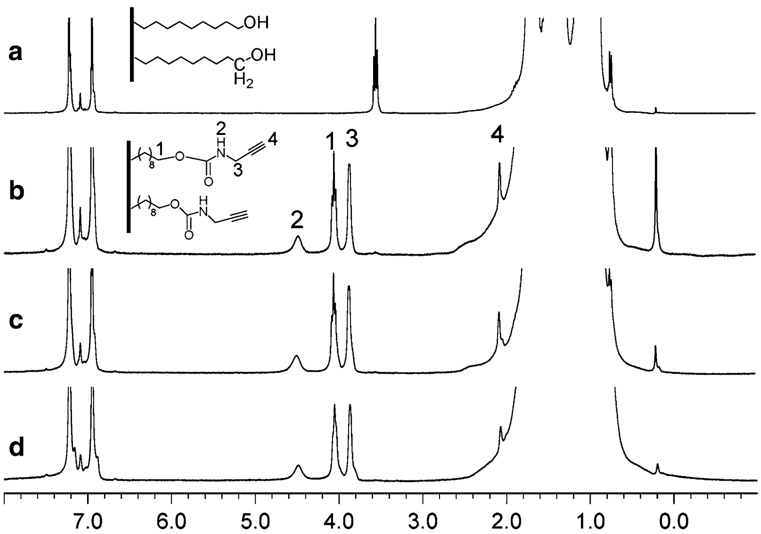


Fig. 1 ^{1}H NMR results of iPP-g-OH and iPP-g-≡ with different M_w: **a** iPP-g-OH-1; **b** iPP-g-≡-1 from iPP-g-OH-1; **c** iPP-g-≡-2 from iPP-g-OH-2; and **d** iPP-g-≡-3 from iPP-g-OH-3

Cotarca et al. [33] reported that BTC can be decomposed quantitatively to phosgene at room temperature by chloride ion. Tetramethylammonium chloride (NMe$_4$Cl) was selected to catalyze the decomposition of BTC to phosgene for the alkyne functionalization of iPP-g-OH. BTC was catalyzed by NMe$_4$Cl to decompose phosgene complete, which reacted in situ with hydroxyl group to produce iPP-g-O-COCl. The excess phosgene was then distilled. In the next step, propargyl amine was introduced to initiate the amidation of –COCl group to produce alkyne-grafted iPP.

All three iPP-g-OH samples were conducted for alkynylation, and the results are shown in Fig. 1. All iPP-g-OH samples were converted to iPP-g-≡ quantitatively, which can be confirmed by the complete disappearance of the methylene group adjacent to –OH at 3.45–3.55 ppm and the appearance of four new peaks. The most exciting part in our experiment is the complete conversion of iPP-g-OH sample with $M_w = 2.88 \times 10^5$, and the molecular weight is so high that it is insoluble even in boiling toluene for several hours and remains as a solid through the whole functionalization process.

Synthesis of long chain branched polypropylene (LCBPP)

The characterization data of samples for synthesis of LCBPP and their click products are summarized in Table 2. A physical blend of iPP-St-N$_3$ and iPP-g-≡ (16/8.5 in weight) was also prepared by refluxing in xylene for 1 h for contrast.

Figure 2 exhibits ^{1}H NMR spectra of reactants and products. The peak at 4.5 ppm of iPP-St-N$_3$ disappears after click reaction and a series of peaks belonging to iPP-g-≡ shifts too. The new peak at 5.6 ppm of LCBPP can be attributed to the

Table 2 Characterization data of reactant for production of LCBPP and their click product

Sample	$[-N_3$ or-$\equiv]/\mu$mol (g polymer)$^{-1}$	$M_w/10^4$	PDI	T_m/°C	ΔH/J g^{-1}
iPP-St-N_3	90	3.74	2.25	123.7	32.0
iPP-g-$\equiv$	190	3.65	3.07	144.1, 149.2	91.3
LCBPP	Not detectable	10.43	6.55	137.2	38.7
iPP-St-N_3/iPP-g-OH = 16/8.5 (m%)	–	3.71	2.30	123.6, 144.2	66.6

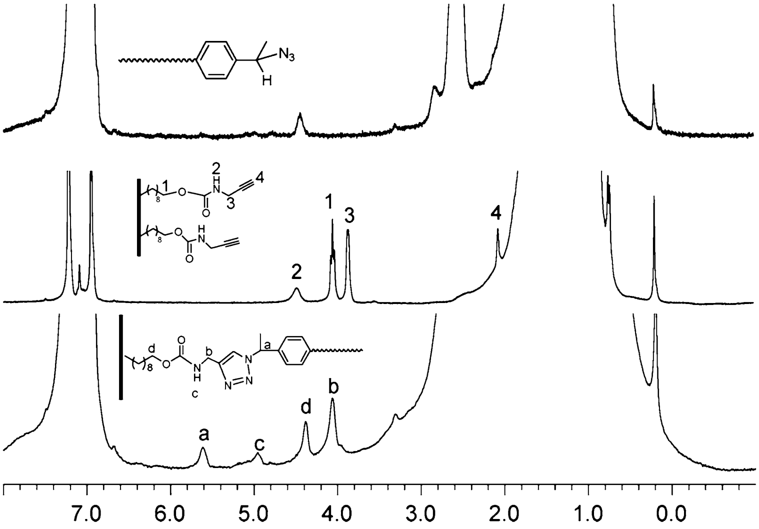


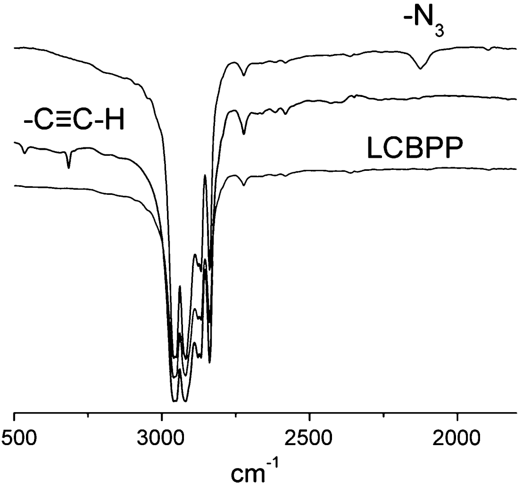
Fig. 2 ^{1}H NMR spectra of iPP-St-N_3, iPP-g-$\equiv$, and LCBPP

proton of the methine group adjacent to the 1,2,3-triazole group [34] and other peaks can also be assigned without a hitch. The combination of two polymer chains can also be characterized visually from FTIR spectra (Fig. 3). Both the signals at 2105 cm^{-1} (assigned to the azide group) and at 3315 cm^{-1} (assigned to the alkyne group) disappears completely in the spectra of LCBPP, indicating the quantitative production of LCBPP (the concentration of excess iPP-g-$\equiv$ is about 7 μmol (g polymer)$^{-1}$ and may not be detected by FTIR).

Figure 4 compares DSC curves of iPP-St-N_3, iPP-g-$\equiv$, LCBPP and blend of iPP-St-N_3/iPP-g-$\equiv$ (16/8.5 in weight). The collected data of melting points (T_m) and thermal enthalpies (ΔH) during melting are listed in Table 2. DSC curve of LCBPP shows only a single peak and is not consistent with the blend of reactants, which shows two distinct peaks attributed to iPP-St-N_3 and iPP-g-$\equiv$, respectively. The difference indicates that LCB structure affects the crystallization behavior of the product.

GPC traces of LCBPP show a remarkable increase in weight-average molecular weight compared with iPP-St-N_3, iPP-g-$\equiv$ and blend of them (Fig. 5). We can calculate from M_w and the concentration of alkyne group [$\equiv$] that there are about

Fig. 3 FTIR spectra of LCBPP and its corresponding azide- and alkyne-functionalized iPP



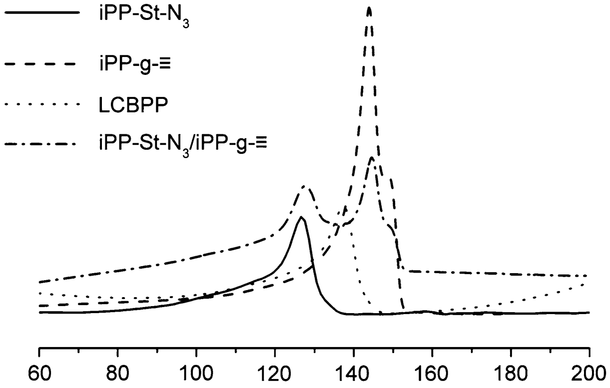


Fig. 4 DSC curves of iPP-St-N_3, iPP-g-≡, LCBPP, and mixtures of iPP-St-N_3/iPP-g-≡ (16/9)

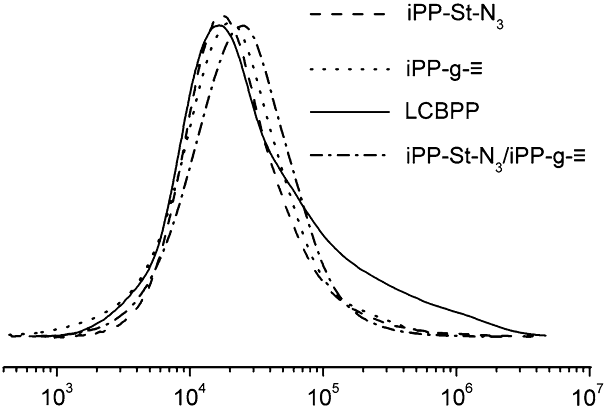


Fig. 5 GPC curves of iPP-St-N_3, iPP-g-≡, LCBPP, and blend of iPP-St-N_3/iPP-g-≡ (16/9)

seven alkyne groups per iPP-g-≡ chain, and after click reaction, at least six of them were transformed to LCB (calculated from the feed ratio of iPP-St-N_3 and iPP-g-≡ as listed in "Experimental part"). Hence the actual molecular weight of LCBPP polymer chain is the sum molecular weight of six iPP-St-N_3 chains and one iPP-g-≡ chain, viz. $(6 \times 3.74 + 3.65) \times 10^4 = 26 \times 10^4$. Since, the radius of gyration for a branched molecule is smaller than that of a linear molecule with the same molecular weight, the molecular weight of LCBPP calculated from GPC with a refractive index detector must be lower than its actual molecular weight, which is consistent with our results as listed in Table 2 (M_w of LCBPP is 10.43×10^4) and implies the formation of LCB structure.

Conclusions

In summary, we have developed a new method to produce LCBPP with well-defined structures (backbone length, graft length, and graft density). Azide-terminated iPP (iPP-St-N_3) was synthesized via the hydrochlorination and subsequent substitution of the starting styryl-terminated-i-PP (i-PP-t-St), which is the product of a metallocene-mediated isospecific propylene polymerization governed by a controlled chain transfer reaction. And the alkyne-functionalized iPP can be produced with high efficiency through one-pot esterification and the subsequent amidation of hydroxyl-functionalized iPP. The click reaction between iPP-St-N_3 and iPP-g-≡ proved to be efficient to obtain LCBPP. The detailed analysis of LCB structures and the construction of other polyolefin-based polymers via click reaction are in progress in our laboratory.

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