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Synthesis of Star Isotactic Polypropylene Using Click Chemistry

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Introduction. Polymers with star-shaped structure containing multiple arms connecting at the central core are among the simplest form of branched topologies. The constant interest in star polymers stems from their unique rheological and mechanical properties and a significantly high degree of functionality.[1] Synthesis of star polymers, especially those of well-defined arm number and length, often utilizes one of two typical approaches: "core-first" by growing arms from a multifunctional initiator;[2] "arm-first" by coupling linear arm precursors onto a multifunctional linking agent.[3] The former approach requiring the use of a multifunctional initiator that can simultaneously initiate multidirectional "living" growth of polymer arms shows much less success compared to the great achievement with the "arm-first" approach.

The "arm-first" approach for the synthesis of well-defined star polymers is developed and widely used by the combination of "living" polymerization techniques, including the traditional "living" anionic and cationic polymerization and the recently developed "living"/controlled radical polymerization (CRP), and the efficient coupling reactions.[4] Among various coupling reactions, the copper(I)-mediated azide−alkyne cycloaddition reaction (CuAAC),[5] which is the most popular click reaction, has gained a great deal of attention due to its extraordinary reliability and functional group tolerance.[6]

Compared to the large number of literatures on synthesis of star polymers from various monomers including styrene and substituted styrenes, methacrylates, and acrylates,[7] the synthesis of star polyolefins is covered by much fewer reports. Polyolefins account for more than half of world production of thermoplastics, which are mostly prepared by the coordination polymerization mechanism.[8] Star polyolefins have been attracting much attention due to the unique rheological properties and that they represent model systems for the research on the relationship between branch structure and performing behavior.[9] However, most studies on star polyolefins are limited to only a few types, that is, star polyisoprene, star polybutadiene, and their hydrogenated polymers, which are prepared by living anionic polymerization of isoprene and butadiene.[10] To date, only one example of the preparation of star polyolefins through the coordination polymerization mechanism was reported by Ye and co-workers.[11] They successfully exploited a novel trinuclear Pd−diimine complex, which enables the "core-first" synthesis of three-arm star polyethylene via ethylene "living" coordination polymerization.

Herein, we demonstrate the first attempt to synthesize star isotactic polypropylene (*i*-PP) by using a combination of propylene coordination polymerization and CuAAC click reaction via the "arm-first" approach. *i*-PP with high azide chain-end functionality prepared via the transformation reaction of the prepolymer (styryl-terminated *i*-PP) is coupled with a trialkyne-containing multifunctional compound under a mild condition to produce three-armed star *i*-PP.

Experimental Details. *Materials and Instruments.* All O_2- and moisture-sensitive manipulations were carried out inside a nitrogen-filled vacuum atmosphere drybox equipped with a dry train. Toluene was deoxygenated by nitrogen purge before refluxing for 48 h and was then distilled over sodium. Methylaluminoxane (MAO, 1.4 M in toluene), which was kindly supplied by CNPC Lanzhou Chemical Co., was dried under vacuum to remove trimethylaluminum (TMA), and the resulting TMA-free MAO (dMAO) was diluted in toluene before use. *rac*-Me_2Si[2-Me-4-Ph(Ind)]$_2ZrCl_2$ (**I**) catalyst was synthesized as described in the literature.[12] The chain transfer agent, 1,2-bis(4-vinylphenyl)ethane (BVPE), was prepared according to the literature.[13] Polymerization-grade propylene was supplied by Yanshan Petrochemical Co. of China. High-purity hydrogen and nitrogen were used as received. CuBr was purified according to a literature procedure.[14] 1,1,2,2-Tetrachloroethane, pentamethyldiethylenetriamine (PMDETA), and *N,N*-dimethylformamide (DMF) were dried over CaH_2 before distillation. All other reagents were used without further purification.

Room- and high-temperature $^1H/^{13}C$ NMR spectra were recorded on Bruker AVANCE 400 and DMX 300 instruments, respectively. FTIR absorbance data were obtained on a Nicolet 6700 FTIR spectrometer. The melting temperature of the polymers was measured by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 instrument controller at a heating rate of 10 °C/min. The molecular weight and molecular weight distribution of 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-3, HT-4, and HT-5 columns. 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 Styryl-Terminated i-PP (*i-PP-t-St*). In a typical reaction (synthesis of *i*-PP1-*t*-St), a Parr 450 mL stainless steel autoclave reactor equipped with a mechanical stirrer was charged with mixed gases of 0.3 bar of hydrogen and 0.7 bar of nitrogen. 32 mL of toluene, 4 mL of dMAO (1.40 M in toluene), and 10 mL of BVPE (0.42 M in toluene) were injected into the reactor and stirred vigorously for 5 min at 30 °C. 2.0×10^{-6} mol of *rac*-Me_2Si[2-Me-4-Ph(Ind)]$_2ZrCl_2$ (**I**) catalyst in toluene solution (1 mL) was then added to the rapidly stirring solution, and 3.0 bar of propylene was fed to initiate the polymerization reaction. Propylene was fed continuously into the reactor to maintain a constant pressure (4.0 bar) during the course of the polymerization. After 15 min of reaction at 30 °C, the reactor pressure was released. The reaction solution was discharged from the reactor and quenched with acidified ethanol. The resulting polymer was filtered off and washed extensively with THF to remove excess BVPE and finally dried under vacuum at 50 °C for 12 h. About 1.80 g of *i*-PP1-*t*-St (containing 0.83 mol % of terminal styryl groups) was obtained.

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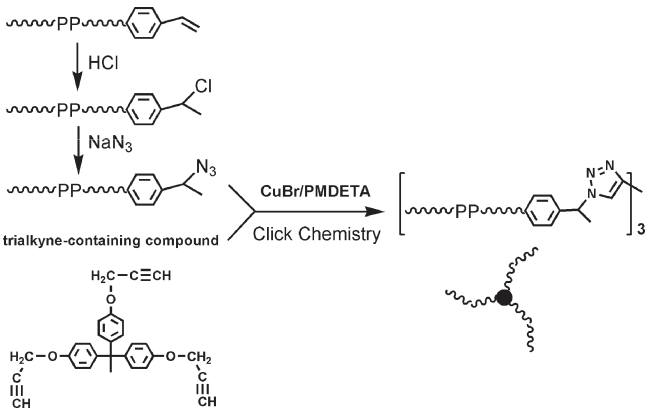
Table 1. Synthesis and Characterization of Styryl-Terminated *i*-PP (*i*-PP-*t*-St)[a]

entry	[BVPE] in feed (mol/L)	yield (g)	[terminal St] (mol %)	M_n (g/mol)	PDI	T_m (°C)	ΔH (J/g)
i-PP1-*t*-St	0.091	1.80	0.86	8150	1.8	135.1/142.3[b]	49.8
i-PP2-*t*-St	0.026	4.75	0.34	24700	1.9	148.6/154.1[b]	77.3

[a] Polymerization conditions: total ~50 mL of toluene, propylene, 4 bar (3.22 mol/L); Cat., 2 μmol; Al/Zr (mol/mol), 3000; H_2, 0.3 bar; temperature, 30 °C; time, 15 min. [b] Dual melting peaks.

Scheme 1. "Click" Synthesis of Three-Armed Star *i*-PP



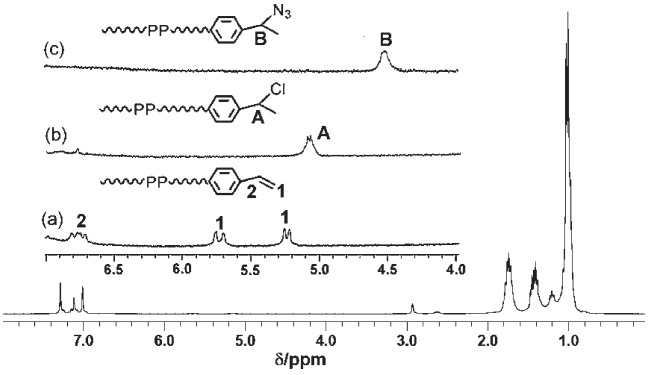


Figure 1. ^{1}H NMR spectra of (a) the starting *i*-PP1-*t*-St (M_n: 0.82×10^4 g/mol), (b) its hydrochlorinated product *i*-PP1-*t*-Cl, and (c) the final terminally azide-functionalized product *i*-PP-*t*-N_3 (solvent: *o*-dichlorobenzene-d_4; temperature: 110 °C).

Hydrochlorination of i-PP-t-St (*Synthesis of i-PP-t-Cl*). In a 250 mL round-bottomed flask equipped with a magnetic stirrer, 1.50 g of *i*-PP-*t*-St polymer was suspended in 80 mL of 1,1,2,2-tetrachloroethane at 60 °C. Dry hydrogen chloride (HCl) that was generated by adding hydrochloric acid (36%) dropwise into concentrated sulfuric acid was bubbled into the suspension. After 8 h, the suspension was poured into 300 mL of ethanol, and the polymer powder was filtered off and dried under vacuum at 50 °C for 12 h.

Preparation of Azide-Terminated i-PP (*i-PP-t-*N_3). In a 250 mL round-bottomed flask equipped with a magnetic stirrer, 1.20 g of *i*-PP-*t*-Cl polymer was dissolved in 80 mL of toluene at 110 °C for 2 h. 20 mL of DMF solution with 0.10 g of NaN_3 was then slowly poured into the toluene solution, and the mixture was stirred for 15 h at 110 °C. The solution was poured into 500 mL of ethanol/water (v/v = 4/1). The white powder was filtered and washed with water and ethanol and finally dried under vacuum at 50 °C for 12 h.

Synthesis of Star i-PP via Azide−Alkyne Click Reaction. In a typical reaction (synthesis of star *i*-PP1), an oven-dried round-bottomed 25 mL flask equipped with a magnetic stirrer and a reflux condenser was charged with 0.25 g of *i*-PP-*t*-N_3, 0.05 mmol of the trialkyne-containing compound, 1,1,1-tris(4-propargyloxyphenyl)ethane, 0.025 mmol of CuBr, and 5 mL of toluene. The mixture was stirred for 2 h at 110 °C. 0.025 mmol of PMDETA was then added to initiate the reaction. After 5 h, the system was poured into acidified ethanol and stirred for 15 min. The resulting product was purified by repeatedly washing with water, acidified ethanol, and water and finally dried under vacuum at 50 °C for 12 h.

Results and Discussion. The click chemistry strategy for the preparation of three-armed star *i*-PP via the "arm-first" method is shown in Scheme 1. In this strategy, azide-terminated *i*-PP (*i*-PP-*t*-N_3) is obtained through the two-step simple and efficient modification, e.g., 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.[13] With a trialkyne-containing multifunctional "core" precursor, 1,1,1-tris(4-propargyloxyphenyl)ethane, and copper(I)-mediated azide−alkyne cycloaddition reaction (CuAAC), three-armed star *i*-PP is expectable.

According to our previous work,[13] *i*-PP-*t*-St with controlled molecular weight can be synthesized through a consecutive chain transfer reaction, first to 1,2-bis(4-vinylphenyl)ethane (BVPE) and then to hydrogen, in propylene polymerization mediated by an isospecific metallocene catalyst (i.e., *rac*-$Me_2Si[2\text{-Me-4-Ph(Ind)}]_2ZrCl_2$) (**I**) activated with methylaluminoxane (MAO)). *i*-PP-*t*-St linear polymers of two different molecular weights ($M_n = 0.82 \times 10^4$ and 2.47×10^4 g/mol) were prepared by varying the concentration of BVPE (Table 1). Both polymers possess typical molecular weight distribution of metallocene-made polyolefins (PDI around 2.0), which is broader than those prepared by "living" polymerization techniques (PDI ≈ 1.0). Figure 1a shows the ^{1}H NMR spectrum of the lower molecular weight *i*-PP1-*t*-St. The peaks at δ = 5.2, 5.7, and 6.8 ppm assigned to the terminal styrenic vinyl groups are clearly observed, while no peaks are attributed to chain end vinyl or vinylidene groups (via β-H or β-CH_3 elimination), which indicates a high selectivity of the styryl chain-end functionality. The ^{13}C NMR spectrum (see Supporting Information) of *i*-PP1-*t*-St shows that there are two types of structures at the beginning of polymer chain (*n*-propyl and 2,3-dimethylbutyl) due to the initiation reaction of Zr−H with 1,2- and 2,1-insertions of propylene. The sum content of *n*-propyl and 2,3-dimethylbutyl is found to be in great accordance with that of the 5-phenyl-2-methylpentyl sequence (resulting from BVPE 2,1-insertion followed by hydrogen chain transfer) subtracting the 2-methyl-4-phenylbutyl sequence (resulting only from BVPE 1,2-insertion into metal−hydride species followed by propylene insertion). Note that there are not any chemical shifts for isobutyl group caused by direct chain transfer to hydrogen. These results ensure that styryl group caps each and every *i*-PP chain.

Hydrochlorination of the terminal styryl groups of *i*-PP-*t*-St with dry hydrogen chloride (HCl) was utilized to introduce chlorine atoms at *i*-PP chain ends,[15] which could be easily transformed into azides via nucleophilic substitution,[16] finally resulting in azide-terminated *i*-PP (*i*-PP-*t*-N_3). The successful introduction of the chlorine atom can be confirmed

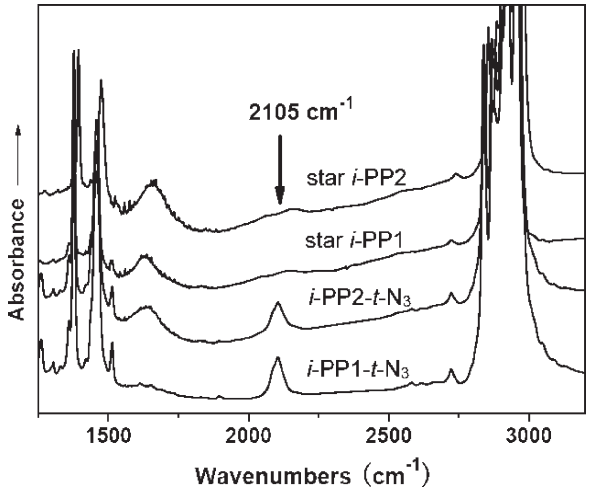


Figure 2. FTIR spectra of the star *i*-PP and their corresponding azide-terminated *i*-PP polymers.

by the complete disappearance of the styrenic vinyl signals at $\delta = 5.2-6.8$ ppm and the appearance of a new peak assigned to the methine group adjacent to the chlorine atom at $\delta = 5.1$ ppm (Figure 1b).

Nucleophilic substitution of the hydrochlorinated *i*-PP was achieved by reaction with NaN_3 in toluene/DMF (v/v = 4/1) mixture at 110 °C for 15 h. A quantitative substitution of the chlorine atom by azide group is supported by observing the shift of the peak assigned to the terminal methine group from $\delta = 5.1$ ppm to $\delta = 4.5$ ppm (Figure 1c). Furthermore, the presence of the azide group in the resultant *i*-PP-*t*-N_3 polymers is characterized by a stretching frequency at 2105 cm^{-1} in the FTIR spectrum (Figure 2).

GPC and DSC curves of the two *i*-PP-*t*-N_3 polymers are compared with those of the corresponding starting *i*-PP-*t*-St polymers in Figures 3 and 4. No marked difference can be discerned from those comparisons. It is worthy to note that dual melting transitions are observed for the obtained *i*-PP. This should be ascribed to the formation of different lamellar thicknesses during crystallization because of the existence of benzene rings inside *i*-PP chain. To the best of our knowledge, this is the first report on the introduction of the highly desirable group, azide group, into *i*-PP macromolecular chain, which implies that CuAAC click reaction would be applicable in the functionalization of PP and synthesis of PP materials with various architectures.[17]

In order to synthesize three-armed star *i*-PP by the CuAAC click reaction with *i*-PP-*t*-N_3, we synthesized a trialkyne-containing compound, 1,1,1-tris(4-propargyloxyphenyl)ethane, via an etherification reaction between 1,1,1-tris(4-hydroxyphenyl)ethane and propargyl bromide according to the literature (see Supporting Information).[18] The CuAAC click reactions were carried out with CuBr/PMDETA as catalyst in toluene at 110 °C. The molar ratio of azide group to alkynyl group was controlled at 1:1 for the high yield of product.[19]

The CuAAC click reaction can be monitored using ^1H NMR. Figure 5 exhibits ^1H NMR spectra of the reaction products of *i*-PP1-*t*-N_3 and 1,1,1-tris(4-propargyloxyphenyl)-ethane at different reaction times. Conversions of azide group are determined by comparing the integrations of the peaks (H_A and H_B) at $\delta = 4.5$ and 5.7 ppm for the unreacted and reacted *i*-PP1-*t*-N_3. After only 20 min reaction, two weak yet clear signals at $\delta = 5.7$ and 5.2 ppm are detected (Figure 5b), which represent the protons (H_B and H_C) of the methine and methylene groups adjacent to the 1,2,3-triazole group,

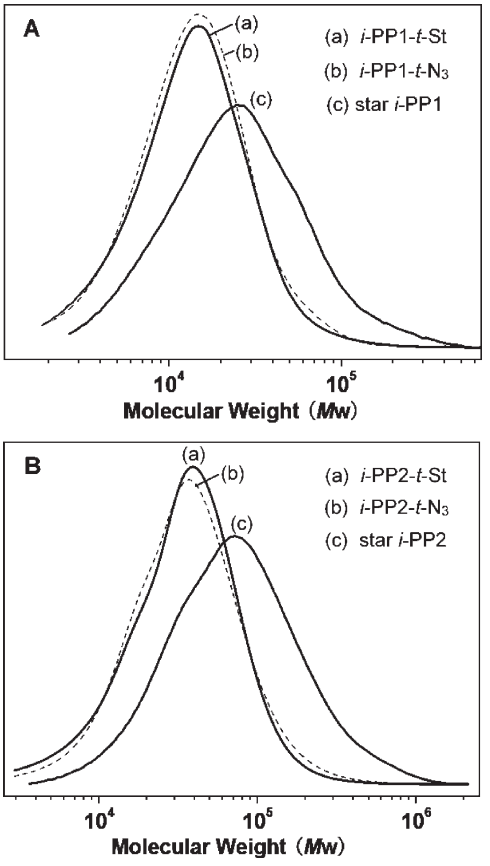


Figure 3. GPC curves of the star *i*-PP and their corresponding azide- and styryl-terminated *i*-PP polymers.

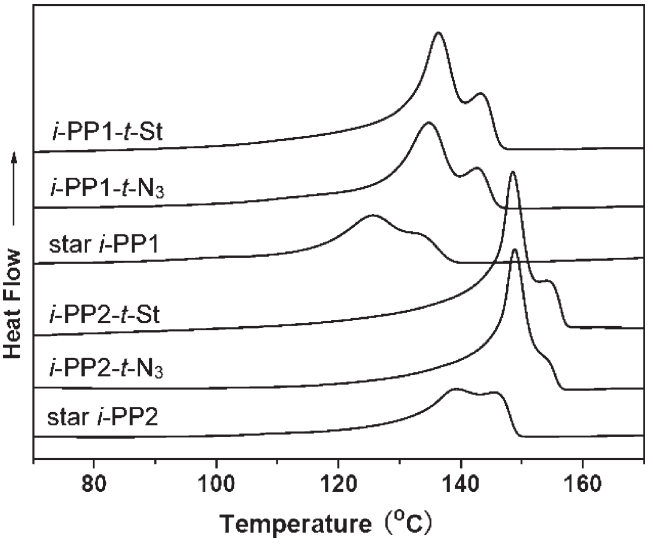


Figure 4. DSC curves of the star *i*-PP and their corresponding azide- and styryl-terminated *i*-PP polymers.

respectively, and the conversion of azide group reaches around 25%. With the reaction progressing, peaks of H_B and H_C gradually strengthen themselves, while the H_A peak is continually weakened. More than 80% of the azide groups have reacted with the alkynyl groups and formed 1,2,3-triazole after 1 h. These results clearly indicate that the CuAAC click reaction between *i*-PP1-*t*-N_3 and 1,1,1-tris(4-propargyloxyphenyl)ethane is highly efficient. Presumably all *i*-PP1-*t*-N_3 polymer chains have been consumed and converted into the

Table 2. Synthesis and Characterization of Three-Armed Star *i*-PP[a]

	i-PP-*t*-N_3						
entry	mass (g)	[N_3] (mmol)	trialkyne[b](mmol)	M_n (g/mol)	PDI	T_m (°C)	ΔH (J/g)
star *i*-PP1	*i*-PP1-*t*-N_3/0.25	0.05	0.05	15 100	2.5	125.8/133.8[c]	34.7
star *i*-PP2	*i*-PP2-*t*-N_3/0.25	0.02	0.02	46 200	2.5	139.2/145.6[c]	57.8

[a] Condition of synthesis of star *i*-PP: [CuBr]/[PMDETA]/[azide group]/[alkyne group] = 0.5/0.5/1/1; toluene, 5 mL; temperature, 110 °C; time, 5 h. [b] 1,1,1-Tris(4-propargyloxyphenyl)ethane. [c] Dual melting peaks.

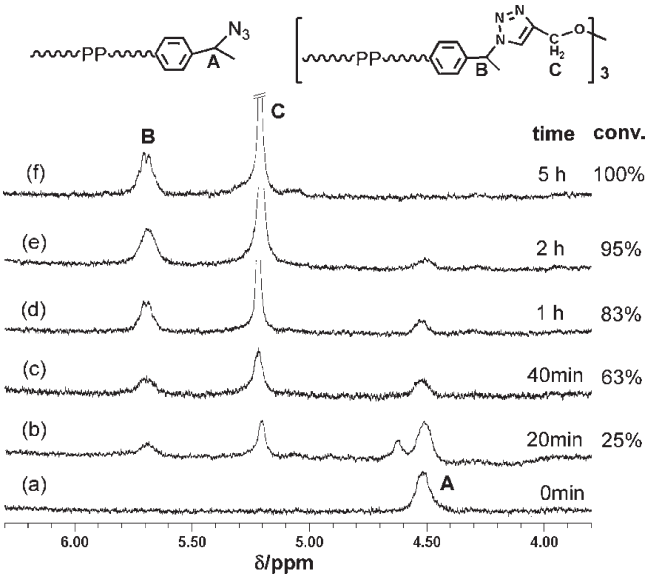


Figure 5. ^{1}H NMR examination of the reaction process between *i*-PP1-*t*-N_3 and 1,1,1-tris(4-propargyloxyphenyl)ethane: (a) 0 min, (b) 20 min, (c) 40 min, (d) 1 h, (e) 2 h, and (f) 5 h (solvent: *o*-dichlorobenzene-d_4; temperature: 110 °C).

arms of star *i*-PP1 within 5 h, as supported by the disappearance of the peak (H_A) at δ = 4.5 ppm in the ^{1}H NMR spectrum of the 5 h reaction product (Figure 5f). Likewise, the other higher molecular weight *i*-PP2-*t*-N_3 sample (M_n = 2.47×10^4 g/mol) can also react with 1,1,1-tris(4-propargyloxyphenyl)ethane to produce three-armed star *i*-PP2 with longer arms (Figure 6).

The synthesis of the three-armed star *i*-PP polymers was further confirmed by FTIR, GPC, and DSC analyses. Figure 2 also displays FTIR spectra of the two star polymers alongside the corresponding *i*-PP-*t*-N_3 polymers. The signal at 2105 cm^{-1}, assigned to the azide group, disappears completely in the spectra of the star polymers, indicating that the CuAAC click reaction must have consumed all of the azide groups. Moreover, GPC traces of the star polymers included in Figure 3 remarkably shift toward higher molecular weight direction without forming an obvious shoulder peak. In addition, the molecular weight distributions of the star polymer are somewhat broader (PDI $\approx$ 2.5) than those of the corresponding *i*-PP-*t*-N_3 polymers (PDI $\approx$ 2.0). This result may suggest the inhomogeneity of the star polymers as the starting "arm" polymers (both *i*-PP-*t*-St and *i*-PP-*t*-N_3) are not of uniform or very narrow-distributed molecular weights. It may also indicate that unreacted i-PP-t-N_3 and some byproduct, e.g., two-arm polymers, exist in the products, which is unavoidable in the "arm-first" approach for the synthesis of star polymers. Nonetheless, star-structured i-PP was mostly prepared by using click chemistry as the coupling reaction, which was supported by ^{1}H NMR, FTIR, and GPC-IR analysis. A detailed characterization of product's absolute molecular weight is in progress by GPC-LALLS.

Figure 4 compares DSC curves of the star polymers with their corresponding *i*-PP-*t*-N_3 arms as well as the starting

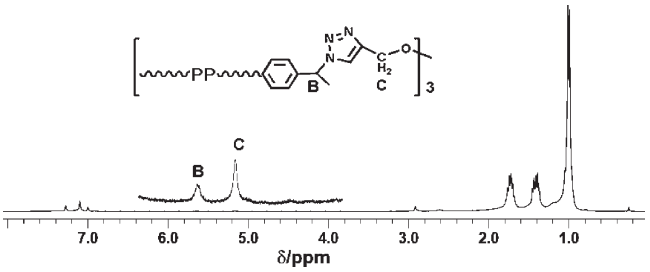


Figure 6. ^{1}H NMR spectrum of the star *i*-PP2 polymer (solvent: *o*-dichlorobenzene-d_4; temperature: 110 °C).

i-PP-*t*-St polymers. The collected data of melting points (T_m) and thermal enthalpies (ΔH) during melting are listed in Table 2. DSC curves of the star polymers are not consistent with those of the starting arm polymers. They show remarkable decreases in both melting point and thermal enthalpy. These decreases can be reasoned by the existence of the core in the star polymer causing crystalline imperfections.

Conclusion. In conclusion, we have demonstrated the synthesis of a new star polymer, star *i*-PP, by using the "arm-first" coupling method. This includes the first preparation of azide-terminated *i*-PP linear polymers through the two-step simple and efficient modification of the starting styryl-terminated *i*-PP, which were obtained by the controlled chain transfer reaction in propylene coordination polymerization. The click reaction between azide-terminated *i*-PP and the trialkyne-containing compound, 1,1,1-tris(4-propargyloxyphenyl)ethane, proved to be efficient to form three-armed star *i*-PP polymers. The present work, thus, has proposed a feasible method for the preparation of star polyolefins by combining olefin coordination polymerization and click chemistry.

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Supporting Information Available: Experimental procedures and characterization of 1,1,1-tris(4-propargyloxyphenyl)ethane, ^{13}C NMR spectrum, and structure illustration of a styryl-capped *i*-PP polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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