

Synthesis of Star-like Polybutadienes by a Combination of Living Anionic Polymerization and “Click” Coupling Method*

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Abstract Three-arm and four-arm star-like polybutadienes (PBds) were synthesized via the combination of living anionic polymerization and the click coupling method. Kinetic study showed that the click reaction between the azido group terminated PBd-t-N₃ and the alkyne-containing multifunctional linking reagent was fast and highly efficient. All coupling reactions were fully accomplished within 40 min at 50 °C in toluene in the presence of the reducing agent Cu(0), proven by ¹H-NMR, FTIR and GPC measurements. For the coupling reactions between the PBd-t-N₃ polymer and dialkyne-containing compound, the final conversion of the coupled PBd-PBd polymer was ca. 97.0%. When a PBd-t-N₃ polymer was reacted with trialkyne-containing or tetraalkyne-containing compound, the conversion of three-arm or four-arm PBd was around 95.5% or 87.0%, respectively. Several factors influencing the coupling efficiency were studied, including the molecular weight of the initial PBd-t-N₃, arm numbers and the molar ratio of the azido group to the alkynyl group. The results indicated that the conversion of the target products would be promoted when the molecular weight of the PBd-t-N₃ was low and the molar ratio of the azido to alkynyl groups was close to 1.

Keywords: Polybutadiene; Living anionic polymerization; Click chemistry; Kinetic study; Coupling efficiency; Star-like.

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INTRODUCTION

A star-like polymer is defined as nonlinear polymer containing multiple arms connecting at a central core, which is the simplest form among branched topologies^[1, 2]. The continuing interest in star-like polymers arises from their compact structure and globular shape relative to their linear analogues with similar molecular weight due to their high segment density, which shows unique self-assembly and rheological behaviors^[3–7]. Most established synthesis approach for star-like polymers is to link chlorosilane compounds with arm precursors based on living anionic polymerization^[8–13]. Typically, three-arm star-like polybutadienes (PBds) were obtained via coupling the macroanions with methyltrichlorosilanes^[14]. Certainly, control over the arm numbers can be achieved by modification of the number of chlorosilanes of the core^[15–17]. However, in order to complete the coupling reaction, extended reaction time and tedious fractionation are often needed. Additionally, the steric hindrance should also be considered. For the preparation of star-like polystyrene/polyisoprene ((PS)_n(PI)_n) copolymers, the

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coupling time could be as long as 1.5–2 months when the functionalities reached to $16^{[18]}$. Besides chlorosilane compounds, chloromethyl^[19] and bromomethyl benzenes^[20] can also be used as the linking reagents, but side reactions such as metal-halogen exchange happened, which significantly lowered the yield of star-like polymers. For pursuing the absolute control of the functionalities, a robust, efficient, and orthogonal protocol is required for synthesis of the star-like polymers in the most efficient way. Recently, the “click chemistry” concept as termed by Sharpless^[21] has attracted numerous attentions in polymer science, due to its ideal features of quantitative yields, simple purification procedures, modularity, width of application, functional group tolerance, and high specificity. The most widely employed click chemistry is based on Cu(I)-catalyzed (3 + 2) Huisgen cycloaddition reaction between the terminal alkyne and azide groups to form 1,4-substituted 1,2,3-triazole^[22–24]. Recent progress^[25–27] in click reaction indicates that it is a strong and versatile tool for the synthesis of functional materials^[28, 29], bioconjugated polymers^[30] and polymers containing complex topological structures^[31–35]. Matyjaszewski and Gao first synthesized tri- and tetra-arm star-like PS by click coupling reaction between the multifunctional core and the azido-group terminated PS synthesized by atom transfer radical polymerization. The yield can reach 90% and 83% for tri- and tetra-arm products within 3 h, respectively^[36]. Tunca also synthesized A_3 -type star-like polymers *via* click chemistry, the conversion could reach 87% for PS in 24 h^[37]. Furthermore, more complex star-like macromolecules can also be synthesized using click coupling reactions^[38–48]. More recently, 3-arm, 6-arm, and 12-arm PS and PEG were synthesized *via* click coupling reactions between azido precursors and dendritic alkyne-containing cores. In particular, the perfect star polymers were identified through MALDI-TOF^[49].

In this work, we explore the synthesis of well-defined star-like PBds. Through taking advantage of perfect control on molecular weight and molecular weight distribution of functionalized precursors *via* living anionic polymerization technique, and click modular criterion, the star-like PBds with predesigned architectures and molecular weight distribution will be expected to obtain in a well controlled fashion.

EXPERIMENTAL

Materials

Butadiene (Yanshan Petrochem. Co., China, polymerization grade) was condensed in a flame-dried flask prior to use. Ethylene oxide (EO) was dried by CaH_2 for 48 h and distilled under N_2 before use. Solvents cyclohexane, methylene chloride, N,N -dimethylformamide (DMF) were dried over activated 0.4 nm molecular sieve before use. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl under N_2 and freshly distilled prior to use. *sec*-Butyllithium (*sec*-BuLi, Acros Organics), 2-bromoisobutryl bromide (98%, Aldrich), propargyl bromide (80% (W/W) toluene solution), N,N,N',N',N'' -pentamethyldiethylenetriamine (PMDETA, Aldrich), CuBr (99%, Aldrich), copper powder (Cu, 99%, Aldrich), 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A, Aldrich), 18-crown-6 ($\geq 99\%$, Aldrich), 1,1,1-tri(4-hydroxyphenyl)ethane (99%, Aldrich), 4-pentynoic acid (Aldrich), sodium azide (NaN_3 , Fuchen Chemical Reagent Factory, China, analytical reagent), 4-(N,N -dimethylamino)pyridine (Aldrich), N -(3-(dimethylamino)propyl)- N' -ethylcarbodiimide hydrochloride (J&K) were used as received. And other reagents were all purchased from Beijing Chemical Plant, China, and purified by standard methods.

Synthesis of Hydroxyl-terminated Polybutadiene (PBd-t-OH)

The polymerizations of butadiene were carried out in all-glass reactors using *sec*-BuLi as initiator *via* schlenk techniques at 40 °C. Chain end hydroxylation was completed by reacting poly(butadienyl)lithium (PBdLi) with 4 equiv. of ethylene oxide ($[\text{EO}]/[\text{PBdLi}] = 4$) overnight at room temperature. The reaction was terminated by freshly distilled degassed 2-propanol and the samples were precipitated in methanol, collected then dried in vacuo at 40 °C for 48 h.

Synthesis of α -Bromoisobutyrate End-capped Polybutadiene (PBd-t-Br)

PBd-t-Br was prepared by esterification of PBd-t-OH with 2-bromoisobutryl bromine. In a typical procedure, PBd-t-OH (11.2 g, 7.2 mmol OH, vacuum-dried at 40 °C overnight immediately prior to use) and triethylamine

(5 mL) were dissolved in 100 mL anhydrous methylene chloride, then cooled to 0 °C in an ice-bath. 2-Bromoisobutyryl bromide (4.4 mL, 36.0 mmol) was then added dropwise to the above solution within 30 min with magnetic stirring. The reaction temperature of the mixture solution was maintained at 0 °C for 2 h and then slowly increased to ambient temperature, after which the reaction was continued for 22 h. After filtration to remove the solid, the resulted brown solution was concentrated by rotary evaporator, precipitated in a mixed solvent methanol/water (V/V = 4/1). The final product was purified by dissolution-precipitation thrice with methylene chloride and methanol/water then dried at 40 °C in vacuum for 48 h.

Synthesis of Polybutadiene with Terminated Azido Group (PBd-t-N₃)

PBd-t-N₃ was obtained by a nucleophilic substitution with sodium azide. Typically, dried PBd-t-Br (9.5 g, 5.6 mmol) was dissolved in THF/DMF (75 mL, V/V = 4/1), then NaN₃ (3.64 g, 56.0 mmol) was added and stirred for 24 h at 50 °C. After filtration to remove the solid, the solution was concentrated by rotary evaporation. The resulting polymer was isolated by precipitation into methanol/water (500 mL, V/V = 4/1) thrice then dried at 40 °C under vacuo for 48 h.

Synthesis of Dialkyne-containing Coupling Agent (1)

In a clean, dry round-bottom flask fitted with a magnetic stirrer and condenser, 18-crown-6 ether (2.31 g, 8.77 mmol) and K₂CO₃ (12.12 g, 87.72 mmol) were added into a solution of 2,2-bis(4-hydroxyphenyl)propane (5.0 g, 21.93 mmol) in acetone (120 mL), followed by adding propargyl bromide solution (8.37 mL, 87.72 mmol). After heating under reflux for 48 h the reaction mixture was filtered. Colorless crystal product could be obtained by chromatographic column (ethyl acetate/petroleum ether 2:10). ¹H-NMR (400 MHz, CDCl₃, δ): 7.16–7.14 (d, 4H), 6.88–6.86 (d, 4H), 4.66–4.65 (d, 4H), 2.51–2.50 (t, 2H), 1.63 (s, 6H).

Synthesis of Trialkyne-containing Coupling Agent (2)

The synthesis and postpurification procedures for coupling agent **2** were similar to those of **1**, except that 1,1,1-tri(4-hydroxyphenyl)ethane (5.0 g, 16.32 mmol) was used to react with propargyl bromide solution (5.36 mL, 53.86 mmol). The product was obtained as white powder. ¹H-NMR (400 MHz, CDCl₃, δ): 7.01–6.99 (d, 6H), 6.88–6.85 (d, 6H), 4.67–4.66 (d, 6H), 2.53–2.52 (t, 3H), 2.11 (s, 3H).

Synthesis of Tetraalkyne-containing Coupling Agent (3)

A clean, dry round-bottom flask containing anhydrous methylene chloride (80 mL) was cooled to 0 °C in ice-water bath. The solvent was purged with N₂ for 30 min before *N*-(3-(dimethylamino)propyl)-*N'*-ethylcarbodiimide hydrochloride (0.700 g, 3.65 mmol), pentaerythritol (0.104 g, 0.761 mmol) and 4-pentynoic acid (0.358 g, 3.65 mmol) were added sequentially. Under magnetic stirring, 0.446 g 4-(*N,N*-dimethylamino)pyridine in 10 mL anhydrous methylene chloride was added into this mixture within 5 min. The reaction mixture was allowed to stir for 40 h at room temperature before washing thrice successfully with 300 mL of 1 mol/L HCl solution, 300 mL of 1 mol/L NaOH solution, and 200 mL NaCl solution. The organic layer was dried with anhydrous MgSO₄ overnight before the solvent was removed in vacuo, yielding **3**. ¹H-NMR (400 MHz, CDCl₃, δ): 4.23 (s, 8H), 2.65–2.50 (m, 16H), and 2.00 (t, 4H).

Synthesis of Linear and Star-like PBds by Click Coupling Reactions

The click coupling reaction between PBd-t-N₃ and coupling agent was conducted in a 50 mL round-bottom flask which was fitted with a magnetic stirrer and a condenser, toluene as solvent and CuBr/PMDETA as catalyst. In a typical procedure of the reaction between PBd-t-N₃ and coupling agent (**1**), PBd-t-N₃ (2.5 g, 1.5 mmol), 2,2-di(4-propargyloxyphenyl)propane (0.23 g, 0.74 mmol), CuBr (0.21 g, 1.5 mmol), Cu (0.095 g, 1.5 mmol) were added sequentially into the round-bottom flask, the flask was deoxygenated by three freeze-pump-thaw cycles before deoxygenated toluene (10 mL) was injected with a syringe. Then the flask was immersed in an oil bath at 50 °C and the mixture was stirred vigorously for 30 min. PMDETA (0.63 mL, 3.00 mmol) was then added to initiate the reaction, and the solution turned to light green color immediately. Samples were withdrawn periodically for GPC analysis. After 3 h, the polymer solution was exposed to air, diluted with THF, and passed through the neutral alumina column to remove the copper catalyst. The solvent was removed in vacuo, then the

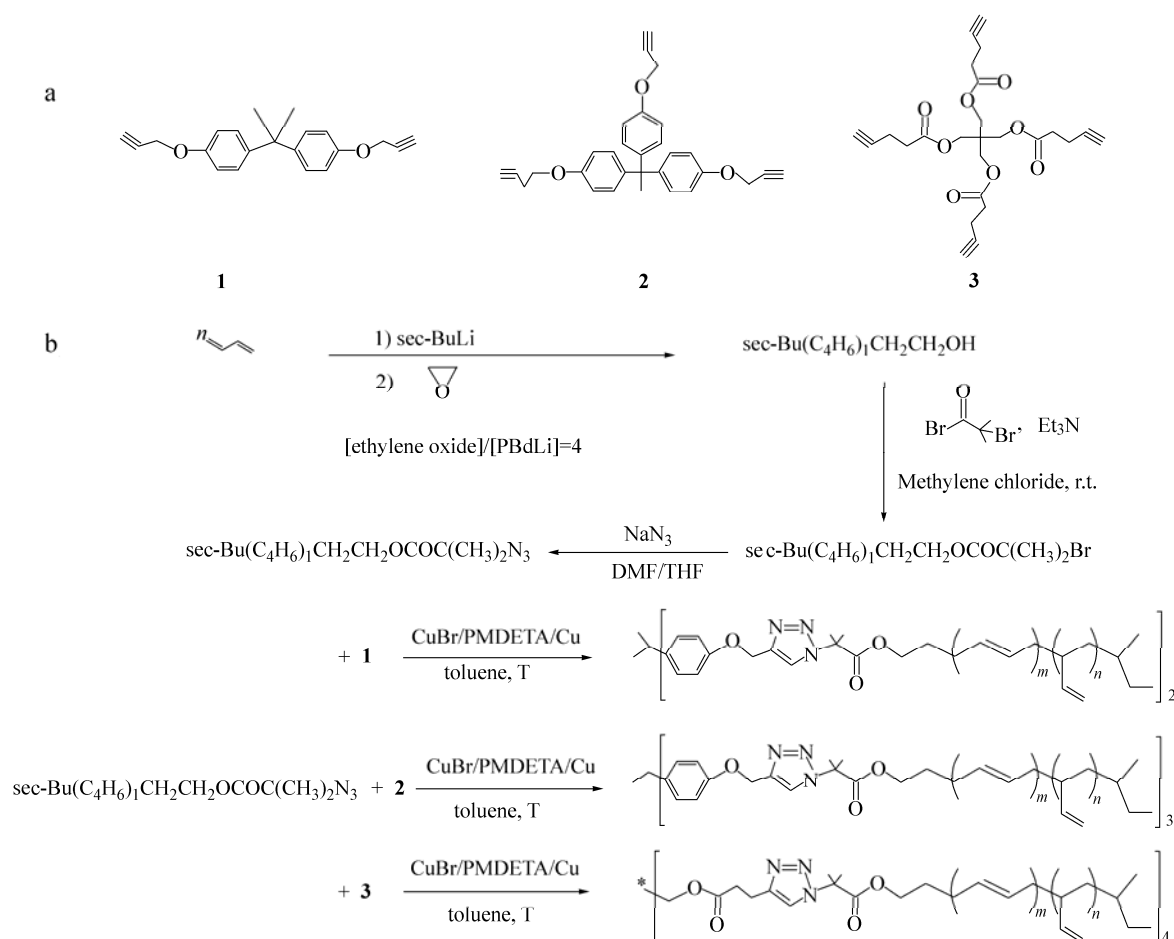
product was precipitated in methanol/water ($V/V = 4/1$) and dried under vacuum at 40 °C for 48 h. The procedure of the reaction of PBd-t- N_3 with different molecular weights and multifunctional coupling reagents (**2**) (**3**) was similar to those of (**1**). Additionally, almost each coupling reaction was completed within 40 min in the presence of the reducing reagent Cu(0).

Characterization

NMR spectra were performed on a Bruker AV300 (400) spectrometer by using $CDCl_3$ as a solvent. Molecular weights were determined by gel permeation chromatography (GPC) on a TOSOH HLC 8220 GPC at 40 °C using THF as an eluent against linear polystyrene standards. Fourier transform infrared (FTIR) spectra were measured on a Perkin Elmer SpectrumOne FTIR spectrometer. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Bruker autoflex III mass spectrometer (Bremen, Germany). The ions were accelerated with pulsed ion extraction by a voltage of 20 kV and detected using a microchannel plate detector. Samples were dissolved in $CHCl_3$, TPB (1,1,4,4-tetraphenyl-1,3-butadiene) was used as the matrix material and silver trifluoroacetate as the ionized reagent.

RESULTS AND DISCUSSION

The click chemistry strategy for the preparation of star-like PBds via the “coupling onto” method is shown in Scheme 1. In this strategy, PBd-t- N_3 was obtained through two-step reactions, *e.g.* esterification of the starting



Scheme 1 (a) Structures of dialkyne-containing (**1**), trialkyne-containing (**2**), tetraalkyne-containing (**3**) compounds, and (b) schematic illustration of synthesis of linear, 3-arm, 4-arm star-like PBds by click reactions

PBd-t-OH and subsequent simple nucleophilic substitution by sodium azide (NaN_3). Here, PBd-t-OH was the product of the functionalization of PBdLi with ethylene oxide^[50]. The expectable products, such as linear, three-arm and four-arm star-like PBds, were obtained via the reaction between PBd-t- N_3 and alkyne-containing multifunctional “core” precursor (1, 2 or 3 shown in Scheme 1a) in the presence of copper(I)-mediated azide-alkyne cycloaddition reaction (CuAAC).

Synthesis of End-group Functionalized Polybutadienes

Living polymerization offers convenient ways for end-group functionalization by chemical transformation with living species. Nucleophilic ring opening reaction of ethylene oxide by living polymer anion is generally applied to the incorporation of hydroxyl groups. Typical MALDI-TOF mass spectrum (Fig. 1) illustrated the exact formula of ionized PBd-t-OH (entry 1 in Table 1), i.e., $\text{C}_4\text{H}_9(\text{C}_4\text{H}_6)_n\text{CH}_2\text{CH}_2\text{OHAg}^+$, which means perfect end-functionalization with 100% efficiency and monoaddition of ethylene oxide. End-group analysis with ^1H -NMR (Fig. 2a) clearly showed characteristic proton peaks at $\delta = 0.88$ and 3.66 which were respectively assigned to methyl groups from the initiator and the methylene group adjacent to terminal hydroxyl group, with an integration ratio of about 3.0:1.0 as expected. The presence of hydroxyl group was also confirmed by FTIR showing a characteristic band at $3300\text{--}3650\text{ cm}^{-1}$ (Fig. 3a). The synthesized PBd-t-OH showed very narrow molecular weight distribution ($\text{PDI} = 1.04$, typical GPC curve in Fig. 4) and the results in Table 1 showed that the molecular weights and molecular weight distribution could be well controlled via living anionic polymerization.

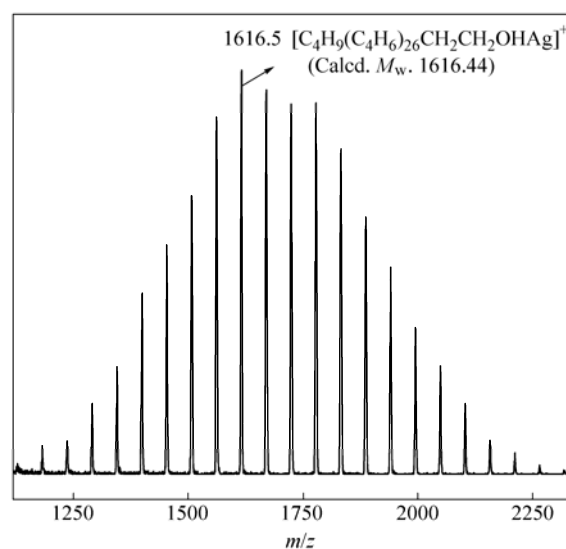


Fig. 1 Representative MALDI-TOF MS spectrum of PBd-t-OH (sample 1 in Table 1)

Table 1. Molecular parameters of PBd-t-OH from the reaction of PBdLi with 4 equiv. of ethylene oxide ($[\text{EO}]/[\text{PBdLi}] = 4$) overnight in cyclohexane at room temperature

Polymer	MALDI-TOF MS		GPC		M_n^a (^1H -NMR)	E.F. ^b (%)
	M_n (g/mol)	PDI (M_w/M_n)	M_n (g/mol)	PDI (M_w/M_n)		
1	1550	1.01	1780	1.04	1540	100
2	1700	1.01	2500	1.05	1560	100
3	2990	1.01	3400	1.03	2870	100
4	5370	1.01	5860	1.02	5000	100
5	10400	1.01	10430	1.02	10050	100

^a M_n is calculated by ^1H -NMR spectroscopy;

^b E.F. is the efficiency of chain ended hydroxyl functionalization measured by MALDI-TOF MS.

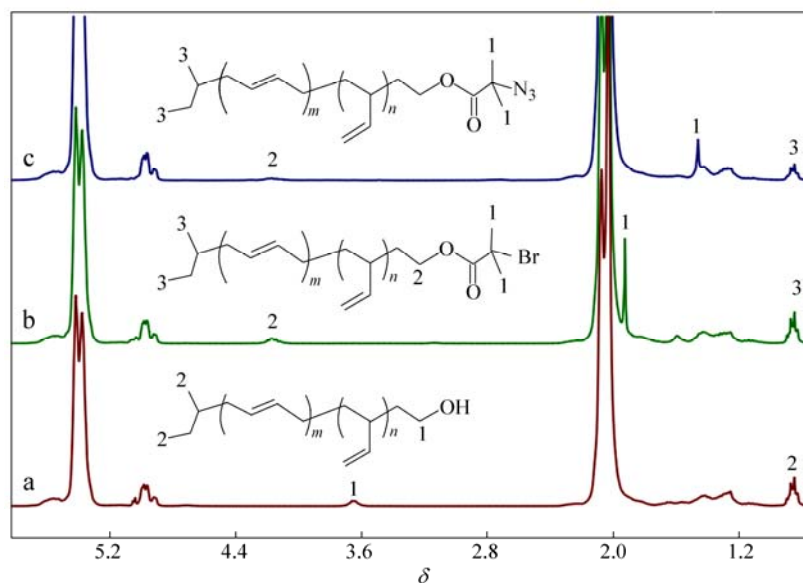


Fig. 2 ^1H -NMR (300 MHz, CDCl_3) spectra of (a) PBd-t-OH, (b) corresponding esterified product PBd-t-Br and (c) subsequent nucleophilic substituted product PBd-t- N_3

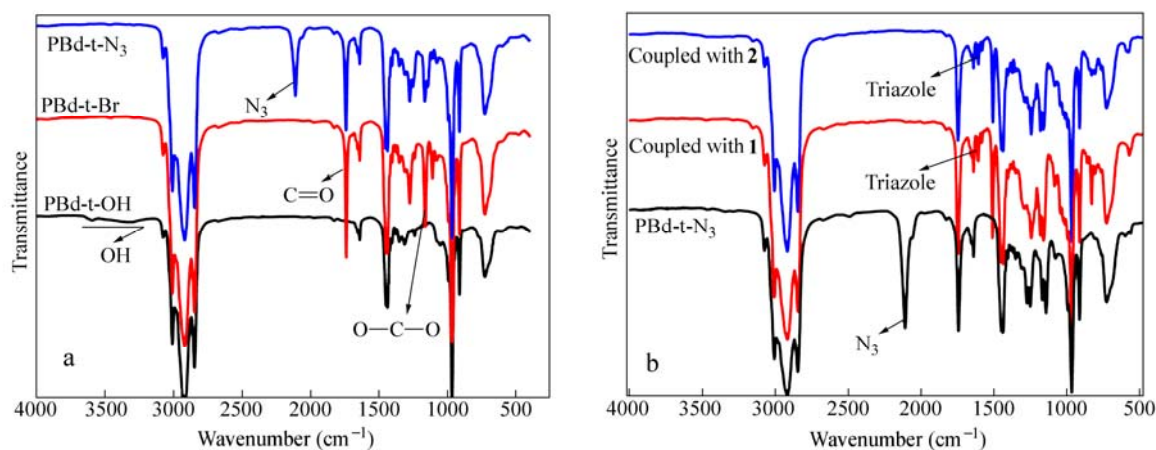


Fig. 3 FTIR spectra of (a) PBd-t-OH, PBd-t-Br and PBd-t- N_3 before click reaction and (b) PBd-t- N_3 , and the corresponding coupling products with coupling reagent **1**, coupling reagent **2**.

Esterification of terminal hydroxyl group with 2-bromoisobutyryl bromide was utilized to introduce α -bromoisobutyrate group at the end of PBd chain, which could be easily transformed into azide groups via simple nucleophilic substitution with sodium azide, finally obtaining PBd-t- N_3 . The successful introduction of α -bromoisobutyrate was confirmed by the complete disappearance of the methylene protons adjacent to hydroxyl group at $\delta = 3.66$ and the appearance of a new peak assigned to the methylene protons adjacent to ester group at $\delta = 4.17$ in ^1H -NMR spectra, and another peak assigned to terminal methyl groups at $\delta = 1.93$ appeared (Fig. 2b). Furthermore, FTIR spectra of the esterification products showed that the signal assigned to the terminal hydroxyl group disappeared completely, and the absorption peaks assigned to the $\text{C}=\text{O}$ at 1740 cm^{-1} and the $\text{O}-\text{C}-\text{O}$ at 1160 cm^{-1} appeared (Fig. 3a). In the GPC elution curve (Fig. 4), symmetric, narrow unimodal peak ($M_n = 1.87\text{ kg/mol}$, $\text{PDI} = 1.04$) was observed in the slightly shorter elution time compared to the starting PBd-t-OH.

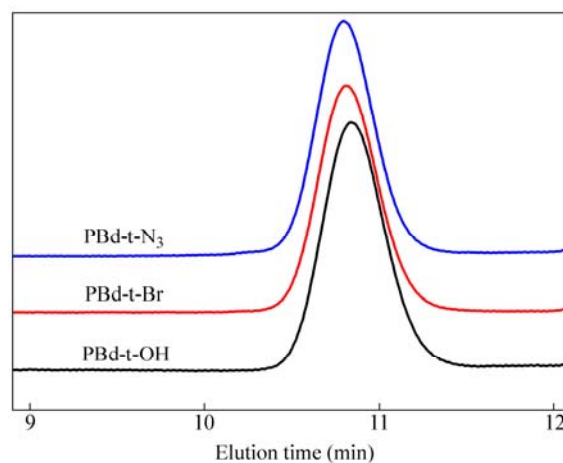


Fig. 4 Typical GPC elution traces of PBd-t-OH (sample 1 in Table 1) and corresponding esterified product PBd-t-Br and subsequent nucleophilic substituted product PBd-t-N₃

PBd-t-N₃ was synthesized by nucleophilic substitution reaction of PBd-t-Br with NaN₃ in THF/DMF (V/V = 4/1) mixture at 50 °C for 24 h. The shift of the peak assigned to the terminal methyl from $\delta = 1.93$ to $\delta = 1.46$ in ¹H-NMR spectra showed the effective substitution of bromine atom by azide group (Fig. 2c). Furthermore, the presence of azide group in the resultant PBd-t-N₃ polymers was also confirmed by a strong absorption peak at 2105 cm⁻¹ in the FTIR spectra (Fig. 3a). Symmetric and narrow single peak ($M_n = 1.9$ kg/mol, PDI = 1.04) was also observed in the GPC elution curve of the resultant PBd-t-N₃ (Fig. 4). All the GPC results of PBd-t-OH, PBd-t-Br and PBd-t-N₃ are summarized in Table S1.

Kinetic Study of Linear and Star-like PBds by GPC

In order to study the effect of steric hindrance on the coupling reaction between alkyne-containing compound and PBd-t-N₃ polymers, the core compounds containing di- (**1**), tri- (**2**) and tetraalkyne group (**3**) were synthesized to utilize in the coupling reaction. Generally, when PBd-t-N₃ with the same molecular weight was coupled with coupling reagents **2** and **3**, the 2-arm PBd would be produced inevitably, therefore the 2-arm PBd via coupling with compound **1** could be used to determine the location of PBd-PBd of the star mixtures in the elution curves of GPC.

The CuAAC click reactions were carried out in toluene with CuBr/PMDETA as catalyst at 50 °C. The reason why toluene is chosen as solvent is that PBd can be dissolving perfectly and the CuBr/PMDETA coordination products can form homogeneous solution in toluene. The reducing reagent Cu(0) was added into each coupling reaction, which could reduce the oxidized Cu(II) species into catalyzed Cu(I) and therefore compensate for the inadvertent oxidation of Cu(I) during coupling reactions, especially in the sampling process for kinetic study^[36].

CuAAC coupling reactions between PBd-t-N₃ ($M_n = 1.66$ kg/mol) and coupling reagent **1** or **2** was monitored by GPC measurements (Figs. 5 and 6). In the coupling reactions between PBd-t-N₃ and compound **1**, the GPC results clearly showed that, in the initial 6 min, the conversion of PBd-PBd coupling products was as high as 91% (Fig. 5b), implying that this reaction was fast and highly efficient, as supported by the disappearance of the elution peak of PBd-t-N₃ precursor mostly (Fig. 5a). After 14 min, the conversion of PBd-PBd increased relatively slowly and reached up to 97% after 45 min. Then the conversion of PBd-PBd almost did not change in spite of extending the reaction time. The left PBd chains, with ca. 3% area fraction through GPC peak splitting using Gaussian functions (Fig. S2), are expected to be a mixture of PBd with azido functionality and PBd chains containing a mono-triazole group at the one chain end. More importantly, the M_w/M_n of the resultant PBd-PBd retained 1.03, as low as that of the starting PBds. In order to clarify the difference in the reaction of synthesizing linear (2-arm) and nonlinear (3-arm) star-like PBd products, the kinetic

study of 3-arm star-like PBds was also carried out using PBd-t-N₃ with the same arm molecular weight to couple with **2** under similar conditions (Fig. 6). In a very short time (8 min), the conversion of 3-arm star-like PBd reached up to 88% and to 95.5% after 40 min. The yield almost unchanged although the coupling time prolonged to 3 h. Generally, when the core was changed from dialkyne to trialkyne containing compound, the process of forming 3-arm star-like products would be difficult due to steric hindrance comparing with the formation of 2-arm products. However, the GPC curves gave the similar results in the initial time. The possible reason is that the arm molecular weight is not high, thus the terminated azide groups of PBd easily contact with alkyne-containing compounds.

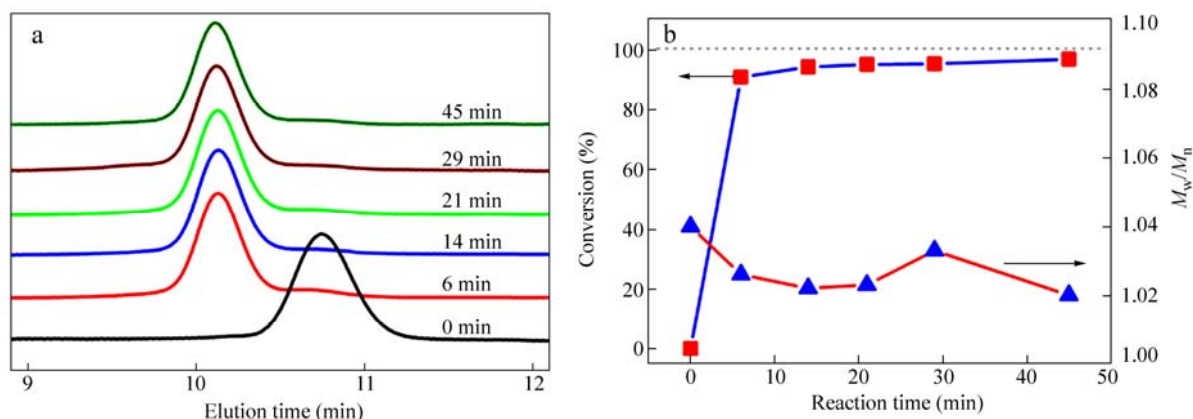


Fig. 5 (a) Evolution of GPC traces of coupling products between PBd-t-N₃ ($M_n = 1.66$ kg/mol) and dialkyne-containing core **1** and (b) the conversion and M_w/M_n of PBd-PBd with extended reaction time

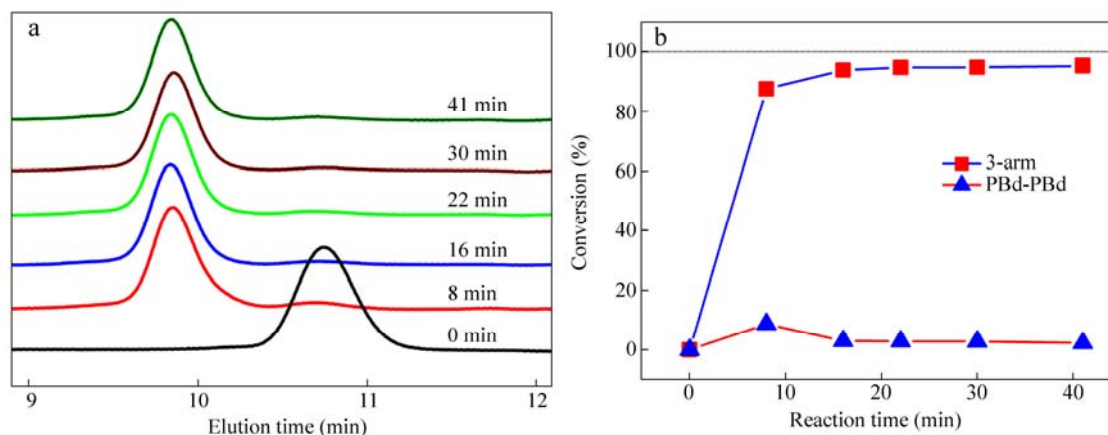


Fig. 6 (a) Evolution of GPC traces of coupling products between PBd-t-N₃ ($M_n = 1.66$ kg/mol) and trialkyne-containing core **2** and (b) the conversion of 3-arm star-like PBd and PBd-PBd with extended reaction time

In order to further explore the initial process of forming star-like PBds, the arm molecular weight was increased to about 3.0 kg/mol. The detailed GPC traces in 10 min are shown in Fig. 7. After 5 min, besides the starting polymers, another overlapping two peaks (2-arm and 3-arm peaks) appeared, and their area ratio was close. It indicated that 2-arm polymer was formed during the coupling reaction, and along with extended reaction time the fractions of 2-arm and starting polymers decreased, the conversion of 3-arm star-like products increased to a constant value.

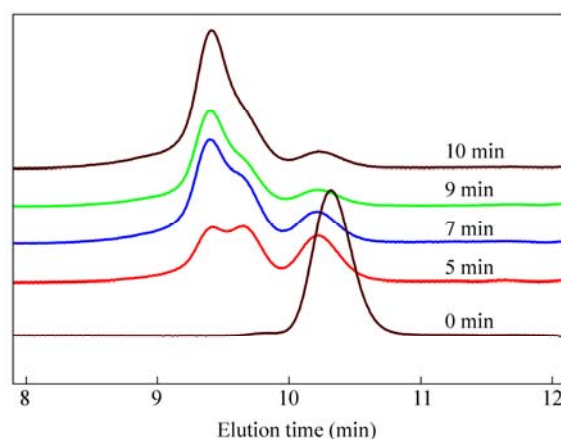


Fig. 7 The initial evolution of GPC traces of coupling reaction between PBd-t-N₃ ($M_n = 3.0$ kg/mol) and trialkyne-containing core 2

The Efficiency of Coupling Reactions

Five samples of PBd-t-N₃ with different molecular weights were used to react with coupling agent **1** using an equimolar ratio of azido to alkynyl groups within *ca.* 40 min. The 40 min was enough for coupling reactions according to the kinetic study. It was supported by the disappearance of the proton peak of $\delta = 1.46$ assigned to the terminated methyl adjacent to azide and the appearance of a new peak at *ca.* $\delta = 1.90$ (Fig. 8A). More importantly, the chemical shift of the characteristic peak $\delta = 7.77$ assigned to the 1,2,3-triazole group was clearly detected. Figure 3(b) also displays FTIR spectra of the coupled products alongside the corresponding PBd-t-N₃. The absorption peak at 2105 cm^{-1} , assigned to the azide groups of PBd-t-N₃, disappeared completely in the FTIR spectra of the coupled polymers, meanwhile, the absorption peak assigned to typical triazole group appeared clearly.

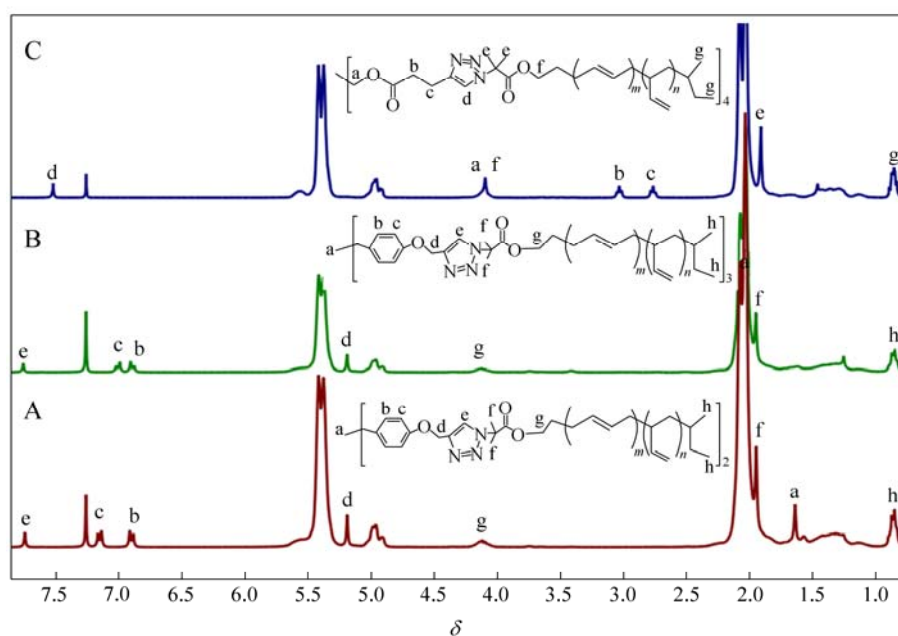


Fig. 8 Typical ¹H-NMR (300 MHz, CDCl₃) spectra of (A) the click reaction products of PBd-t-N₃ with the coupling reagent **1**, (B) with **2** and (C) with **3**.

The results of the click reaction are summarized in Table 2. It was found that increasing the molecular weight of PBd-t-N₃ decreased the final conversion of the resultant PBd-PBd polymer. When the molecular weight of PBd-t-N₃ increased from 1660 g/mol to 5480 g/mol, the conversion of coupled PBd-PBd decreased from 97% to 92%. The possible reasons for the decrease in the coupling efficiency include possible lower azido functionality, unbalanced stoichiometry between the azido and alkynyl groups and the effect of steric hindrance. It is difficult to determine the exact stoichiometry when the mass fraction of the chain end group on the polymer chain is low.

Table 2. GPC characterization of model click reactions between PBd-t-N₃ and coupling reagent 1

	M_n PBd-t-N ₃ (g/mol)	N ₃ /Alkyne (mol/mol)	Area fraction in GPC-RI (%)	
			PBd-PBd	PBd
D1	1660	1/1	97.0	3.0
D2	1800	1/1	96.8	3.2
D3	3100	1/1	92.5	7.5
D4	5480	1/1	92.0	8.0
D5	10500	1/1	75.3	24.7

In the reaction between PBd-t-N₃ and coupling agent 2, when the molecular weight of PBd-t-N₃ was 1660 g/mol, the conversion of the 3-arm star-like product depended on the ratio of the azido group of PBd-t-N₃ to the alkynyl group (Table 3). When the ratio of the azido group of PBd-t-N₃ to the alkynyl group was nearly 1:1, the conversion was ca. 95%. The peak splitting result of the GPC curve indicated that the area ratio of 3-arm star-like, PBd-PBd, mono-PBd chain was 0.955:0.025:0.02 (Fig. S2). It means that ~98% PBd-t-N₃ precursors were coupled with the trialkyne-containing coupling reagent. According to the results from GPC and ¹H-NMR, it was concluded that nearly all the azido groups were nearly quantitatively coupled and converted to the 1,2,3-triazole groups within only 40 min in the case with an equimolar amount of the PBd-t-N₃ and the coupling reagent 2.

Table 3. GPC characterization of 3-arm star-like PBds synthesized by click reactions

	M_n PBd-t-N ₃ (g/mol)	N ₃ /Alkyne (mol/mol)	Area fraction in GPC-RI (%)		
			3-arm star	PBd-PBd	PBd
T1	1660	1/1	95.5	2.5	2.0
T2	1660	1/1.2	84.9	13.5	1.6
T3	1660	1/1.3	67.1	28.7	4.2
T4	1800	1/1	95.4	2.3	2.3
T5	3100	1/1	91.5	1.9	6.6
T6	5480	1/1	88.2	5.9	5.9
T7	10500	1/1	68.8	14.5	16.7

When the stoichiometry of the azido groups and the alkynyl groups was designed to be unbalanced deliberately, such as 1/1.2, or 1/1.3 (entries T2, T3 in Table 3), the ratio of the three species (the 3-arm star-like, the PBd-PBd coupled polymer, the mono-PBd chain) varied correspondingly. This ratio changed in agreement with the theoretical expectations, because the conversion of the 3-arm star-like PBds obviously decreased as the ratio of the azido groups to the alkynyl groups decreased, and the corresponding PBd-PBd coupled polymers increased. For example, when the ratio of azido to alkynyl groups decreased to 1/1.2, the conversion of 3-arm star-like PBds decreased to 85%. Additionally, the conversion of 3-arm star-like PBds was also influenced by the molecular weight of the PBd-t-N₃ chains. It was found that when the molecular weight increased from 1660 g/mol to 5480 g/mol, the conversion of 3-arm star-like polymers decreased from 95% to 88% (Table 3). Furthermore, the conversion of 3-arm further decreased when $M_n = 10$ kg/mol. This is ascribed to that the coupling reaction of PBd-t-N₃ with coupling agents was difficult when PBd-t-N₃ with higher molecular weights was used due to the effect of steric hindrance, and the stoichiometry might be not accurate. The typical FTIR and ¹H-NMR spectra of coupling products are illustrated in Figs. 3(b) and 8(B), respectively. Similarly, the characteristic peak assigned to the 1,2,3-triazole group was obviously seen.

Four-arm star-like PBds were also synthesized by click coupling reactions between the PBd-t-N₃ and the tetraalkyne-containing linking reagent **3**. Table 4 presents the conversion of the coupling products within 40 min. When the molecular weight of PBd-t-N₃ was 1660 g/mol, the area ratio of the four species (4-arm star-like, 3-arm star-like, PBd-PBd and mono-PBd polymer) was 87.0:1.5:0.5:11.0. Moreover, when the molecular weight increased to 5480 g/mol, the conversion of 4-arm star-like polymer decreased to 73.0%. It could also be supported by ¹H-NMR (Fig. 8C) and FTIR measurements.

Table 4. GPC characterization of 4-arm star-like PBds synthesized by click reactions

Coupling agents	M_n PBd-N ₃ (g/mol)	N ₃ /Alkyne (mol/mol)	Area fraction in GPC-RI			
			4-arm star	3-arm star	PBd-PBd	PBd
(3)	1660	1/1	87.0	1.5	0.5	11.0
(3)	5480	1/1	73.0	12.0	4.5	10.5

CONCLUSIONS

Star-like PBds were synthesized by the combination of living anionic polymerization and click chemistry. The results indicated that molecular weight distribution and architectures of the coupled polymers could be well controlled by the combination of living anionic polymerization and click method. Through living anionic polymerization, the arm molecular weight and functionality were controlled accurately. The coupling efficiency was high as 97.0% for PBd-PBd within 40 min. Meanwhile, the conversion for 3-arm star-like PBds was 95.5% which were almost pure star-like PBds. Molecular weight of PBd-t-N₃, the stoichiometry between azide and alkynyl groups and arm numbers influenced the efficiency of coupling reactions between PBd-t-N₃ and coupling reagents. This work provides a new strategy for synthesizing star-like PBds. Our following work will focus on the crystallization^[51] and melt rheological behaviors of hydrogenated star-like products (star-like polyethylene) with the aim of understanding the topological effects on properties.

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