

# Synthesis and Characterization of Star Graft Copolymers with Asymmetric Mixed “V-Shaped” Side Chains via “Click” Chemistry on a Hyperbranched Polyglycerol Core

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**ABSTRACT:** The star graft copolymers composed of hyperbranched polyglycerol (HPG) as core and well defined asymmetric mixed “V-shaped” identical polystyrene (PS) and poly(*tert*-butyl acrylate) as side chains were synthesized via the “click” chemistry. The V-shaped side chain bearing a “clickable” alkyne group at the conjunction point of two blocks was first prepared through the combination of anionic polymerization of styrene (St) and atom transfer radical polymerization of *tert*-butyl acrylate (*t*BA) monomer, and then “click” chemistry was conducted between the alkyne groups on the side chains and azide groups on HPG core. The obtained star graft copolymers and intermediates were characterized by gel permeation chromatography (GPC), GPC equipped with a multiangle laser-light scattering detector (GPC-MALLS), nuclear magnetic resonance spectroscopy and fourier transform infrared. © 2009 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 47: 1308–1316, 2009

**Keywords:** “click” chemistry; graft copolymers; hyperbranched; star polymers

## INTRODUCTION

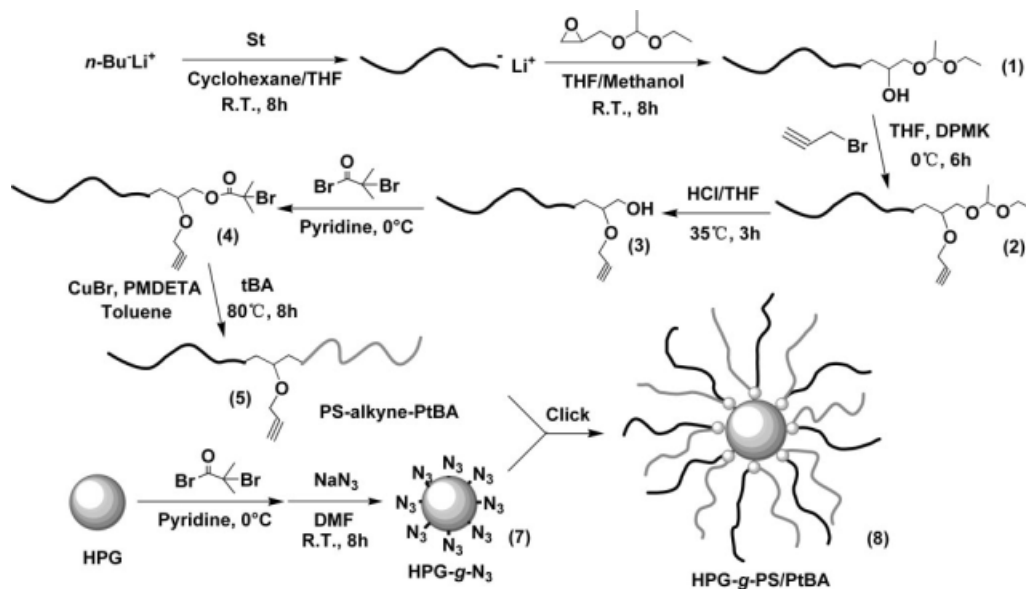
The construction of complex macromolecules exhibiting a precise architecture, size, shape, and functionality is a challenging domain with rapidly growing interest.<sup>1,2</sup> It aroused the incentives in the increasing needs for molecular devices which accompany the development of nanotechnologies. Recently, the key points of investigation were centered on the synthesis of graft polymers with complex architectures because of their important roles in understanding the correlation of structure and properties, and exploring new materials.<sup>3,4</sup> In

particular, the synthesis of graft polymers with two identical side chains at each graft point, named “centipede-like” polymer or “V-shaped” graft polymer, has been reported.<sup>3,4</sup> This kind of copolymers were generally synthesized by “graft onto” method developed by Hadjichristidis<sup>5–7</sup> and Hirao<sup>8,9</sup> using chlorosilane or 1,1-diphenylethylene derivatives as coupling agents respectively, but lately Huang et al.<sup>10</sup> obtained the graft copolymers of polyacrylate as backbone and poly(ethylene glycol), polystyrene (PS) as side chains by combination of “graft through” and “graft from” strategies. Interestingly, Zubarev and coworkers<sup>11–14</sup> synthesized the star-shaped copolymers with the V-shaped poly(butadiene)-poly(ethylene oxide) arms by “graft onto” method and investigated their assemblies. However, for each macromolecule only six arms were coupled onto a small molecule core.

Additional Supporting Information may be found in the online version of this article.

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**Scheme 1.** Stepwise synthesis of “V-shaped” side chain PS-alkyne-*PtBA* and identical star graft copolymers HPG-*g*-PS/*PtBA*.

On the other hand, there are some disadvantages for the preparation of the V-shaped side chains by anionic technology: (i) the linking and purification for each step is a time-consuming process, (ii) the efficiency of the linking reaction is unsatisfactory, which is affected by the steric volume of the linking agent and the macromolecular chain, and (iii) in anionic polymerization for the preparation of the V-shaped side chains, only a limited number of monomers could be used. Thus, looking for a simple and universal method to prepare the graft copolymers with V-shaped side chains would be interesting for polymer chemists. For example, by using the living “controlled” polymerization techniques as the atom transfer radical polymerization (ATRP),<sup>15</sup> nitroxide-mediated radical polymerization,<sup>16</sup> reversible addition fragmentation transfer polymerization (RAFT),<sup>17</sup> and single electron transfer polymerization,<sup>18–21</sup> as well as the “click chemistry,”<sup>22,23</sup> the graft copolymers with complicated structure could be made.

In our previous work, a mixed-arm star polymer hyperbranched polyglycerol-*graft*-polystyrene/poly(*tert*-butyl acrylate) (HPG-*g*-PS/*PtBA*) was synthesized by the “core first” strategy,<sup>24</sup> which can better control over polymer structure than “arm first”<sup>25</sup> or “in-out”<sup>26</sup> methods. However, the numbers of PS and poly(*tert*-butyl acrylate) (*PtBA*) arms are not identical, because the reaction efficiency of RAFT agents with remained hydroxyl groups on hyperbranched polyglycerol (HPG) and then its initiation efficiency for second

arm are affected by steric hindrance of the first arm. Therefore, how to control the identical number of mixed side chains in star graft copolymers is still a challenge.

Herein, a new approach shown in Scheme 1 was presented to prepare star graft copolymers with asymmetric V-shaped side chains of PS and *PtBA* on HPG core, in which the asymmetric V-shaped side chains of PS and *PtBA* with alkyne group at the conjunction point of two blocks were prepared first by the combination of living anionic polymerization and ATRP, then the alkyne group of the V-shaped side chains was further reacted with azide groups on HPG, the star HPG-*g*-PS/*PtBA* were obtained.

## EXPERIMENTAL

### Materials

HPG [ $M_n = 30,000$ , polydispersity index (PDI) = 1.27, 400 hydroxyl groups/HPG] was synthesized and purified according to the previous literature.<sup>27</sup> Styrene (St, >99.5%, Aldrich) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over  $\text{CaH}_2$ , and distilled under reduced pressure. Glycidol (Tech., Acros), 1,1-diphenylmethane (99%), and *tert*-butyl acrylate (*tBA*, Aldrich) were dried by  $\text{CaH}_2$ , then distilled under reduced pressure and stored at  $-20\text{ }^\circ\text{C}$  before use. *N,N*-dimethylformamide (DMF), toluene, cyclohexane, 1-butyl

chloride, ethyl vinyl ether (98%), and propargyl bromide (>99%, Aldrich) were dried by  $\text{CaH}_2$  and distilled just before use. Tetrahydrofuran [THF, 99%, Sinopharm Chemical Reagent Co., (SCR)] and pyridine (99.5%, SCR) were refluxed and distilled from sodium naphthalenide solution and sodium wire, respectively. Copper (I) bromide ( $\text{CuBr}$ , 95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and dried *in vacuo*. Bromoisobutyryl bromide (98%, Aldrich),  $N,N,N',N'',N''$ -penta-methyl diethylenetriamine (PMDETA, Aldrich), formic acid (SCR), sodium azide ( $\text{NaN}_3$ , >98%, SCR), and potassium hydroxide ( $\text{KOH}$ , SCR) were used as received. All other reagents and solvents were purchased from SCR and used as received except for declaration. Diphenylmethyl potassium (DPMK) solution was freshly prepared by the reaction of potassium naphthalenide with diphenylmethane in THF according to the literature,<sup>28</sup> the concentration was 0.61 mol/L. Ethoxyethyl glycidyl ether (EEGE) was synthesized from glycidol and ethyl vinyl ether according to Fitton et al.<sup>29</sup> and distilled under reduced pressure (bp 152–154 °C), and the purity exceeded 99.6 GC%.<sup>30</sup> *n*-Butyl lithium (*n*-BuLi) was prepared according to the literature<sup>31</sup> and analyzed by the double-titration method<sup>32</sup> with the concentration of 1.57 mol/L.

#### Preparation of EEGE-Functionalized Polystyrene (PS-EEGE)

The anionic polymerization of St was carried out under the nitrogen ( $\text{N}_2$ ) atmosphere. Typically, the St (10 mL), cyclohexane (120 mL), and THF (4 mL) were charged into a 500 mL dried ampoule under nitrogen atmosphere, then the *n*-Bu<sup>-</sup>Li<sup>+</sup> solution (2.35 mL, 3.69 mmol) was injected by a syringe under magnetic stirring. The reaction was kept at room temperature for 8 h, then a mixture of EEGE (3.0 mL, 20.55 mmol) and THF (4 mL) was added promptly and the system was stirred for another 8 h before the termination by methanol. After the solvent was evaporated, the product was purified by dissolution/precipitation twice with THF/methanol and the obtained white powder of functionalized polystyrene (PS-EEGE) was dried under vacuum at 45 °C for 24 h to a constant weight of 8.90 g in a yield of 98.0%.

<sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.80 (m,  $\text{CH}_3\text{CH}_2-$ ), 1.13 (m,  $\text{CH}_3\text{CH}_2\text{O}-$ ), 1.22 (m,  $-\text{CH}(\text{CH}_3)-$ ), 1.26–2.01 (m,  $-\text{CH}_2\text{CH}-$  of PS chain), 3.09–3.43 (m,  $\text{CH}_3\text{CH}_2\text{O}-$ ,  $-\text{CH}(\text{OH})\text{CH}_2\text{O}-$ ), 3.52 (m,

$-\text{CH}(\text{OH})-$ ), 4.65–4.76 (m,  $-\text{OCHO}-$ ), 6.30–7.30 (m,  $-\text{C}_6\text{H}_5$  of PS chain).  $M_n(\text{GPC}) = 2300$  g/mol, PDI = 1.04,  $M_n(\text{NMR}) = 2500$  g/mol.

According to the thin layer chromatography results, the  $R_f$  value of functionalized PS-EEGE was 0.23 and the corresponding unfunctionalized PS was 1.00 when toluene was used as the developing agent.<sup>33</sup> Thus, the crude product could be purified by column chromatography using silica gel (200–300 mesh) as filling material and toluene as the first eluent. After the front running of unfunctionalized PS was eluted, the eluent was gradually changed to pure THF to wash out the remaining functionalized PS-EEGE completely.

#### Preparation of $\alpha$ -(*n*-Butyl)- $\omega$ -Propargyl, $\omega'$ -Ethoxyethyl-Polystyrene (PS-alkyne-EEGE (2))

In a 250 mL dried ampoule, 8.0 g dried PS-EEGE [(1),  $M_n(\text{GPC}) = 2300$  g/mol, 3.48 mmol] and 150 mL THF were added. Then, the system was charged with  $\text{N}_2$  and titrated by DPMK solution until the solution changed to reddish-brown. After the ampoule was placed into ice bath, propargyl bromide (2.0 mL, 3.158 g, 26 mmol) was added dropwise for 2 h and the reaction was continued for 24 h at room temperature. The PS-alkyne-EEGE was obtained by the separation of the formed salts and then precipitation in methanol twice, and dried under vacuum at 45 °C for 12 h until a constant weight (7.86 g, 98.3% yield) was obtained.

<sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.80 (m,  $\text{CH}_3\text{CH}_2-$ ), 1.13 (m,  $\text{CH}_3\text{CH}_2\text{O}-$ ), 1.22 (m,  $-\text{CH}(\text{CH}_3)-$ ), 3.09–3.59 (m,  $\text{CH}_3\text{CH}_2\text{O}-$ ,  $-\text{CH}(\text{O}-)\text{CH}_2\text{O}-$ ), 3.84–4.18 (m,  $-\text{OCH}_2\text{C}\equiv\text{CH}$ ), 4.65–4.76 (s,  $-\text{OCH}(\text{CH}_3)\text{O}-$ ). FTIR ( $\text{cm}^{-1}$ ): 3300 ( $-\text{C}\equiv\text{CH}$ ).

#### Preparation of $\alpha$ -(*n*-Butyl)- $\omega$ -Propargyl, $\omega'$ -Hydroxyl-Polystyrene (PS-alkyne-OH (3))

The hydroxyl group was recovered by hydrolysis of ethoxyethyl group at  $\omega$  end of PS-alkyne. Typically, 7.5 g [ $M_n(\text{GPC}) = 2400$  g/mol, 3.13 mmol] PS-alkyne-EEGE (2) was dissolved in 150 mL THF, and then 13 mL HCl (37%) was added and stirred for 2 h at room temperature. The PS-alkyne-OH was obtained by removing the formed salts and precipitation in methanol twice, and dried under high vacuum at 45 °C for 12 h until a constant weight (7.20 g, 96.0% yield) was obtained.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.80 (m,  $\text{CH}_3\text{CH}_2-$ ), 3.09–3.55 (m,  $-\text{CHCH}_2\text{OH}$ ), 3.84–4.18 (m,  $-\text{OCH}_2\text{C}\equiv\text{CH}$ ). FTIR ( $\text{cm}^{-1}$ ): 3300 ( $-\text{C}\equiv\text{CH}$ ).

#### Preparation of $\alpha$ -(*n*-Butyl)- $\omega$ -Propargyl, $\omega'$ -(2-Bromoisobutryl)-Polystyrene (PS-alkyne-Br (4))

In a 250 mL round bottom flask, 7.0 g [ $M_n(\text{GPC}) = 2400$  g/mol, 2.92 mmol] dried PS-alkyne-OH (3) was added and dissolved in 100 mL anhydrous pyridine. The system was placed in ice bath and 1.3 mL (10.5 mmol) 2-bromoisobutryl bromide was added dropwise for 0.5 h. After the solution was stirred for 24 h, the pyridine was evaporated and the polymer was precipitated in methanol twice, dried at 45 °C for 12 h and the PS-alkyne-Br was obtained with the constant weight (6.78 g, 96.9% yield).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.80 (m,  $\text{CH}_3\text{CH}_2-$ ), 1.94 (s,  $-\text{C}(\text{CH}_3)_2\text{Br}$ ), 3.09–3.55 (m,  $-\text{CHCH}_2\text{O}-$ ), 3.84–4.18 (m,  $-\text{CH}_2\text{COO}-$ ,  $-\text{OCH}_2\text{C}\equiv\text{CH}$ ). FTIR ( $\text{cm}^{-1}$ ): 3300 ( $-\text{C}\equiv\text{CH}$ ), 1737 ( $-\text{COO}-$ ).

#### Preparation of Diblock Copolymer Polystyrene-alkyne-Poly(*tert*-butyl acrylate) (PS-alkyne-PtBA(5))

The diblock copolymer of PS-alkyne-PtBA with an alkyne group at the conjunction point was carried out using PS-alkyne-Br (4) as macroinitiator. The procedure was showed as follows: a 50 mL ampoule charged with CuBr (0.143 g, 1.0 mmol), PMDETA (0.346 g, 2.0 mmol), PS-alkyne-Br 2.4 g [ $M_n(\text{GPC}) = 2400$  g/mol, 1.0 mmol], *t*BA (3.71 g, 4.2 mL), and toluene (15 mL) was vacuumed by three freeze-thaw cycles at the temperature of liquid nitrogen, then sealed and placed in an oil bath at 80 °C for 8 h. The copper salts were removed by passing the reacted product through an activated basic alumina column, and then the obtained solution was diluted with THF and precipitated twice in methanol/ $\text{H}_2\text{O}$  system. After filtration, the products of PS-alkyne-PtBA were dried at 45 °C for 12 h until a constant weight (5.20 g, 85.1% yield) was obtained.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.80 (m,  $\text{CH}_3\text{CH}_2-$ ), 0.91–1.20 (m,  $-\text{C}(\text{CH}_3)_2-$ ), 1.26–2.06 (m,  $-\text{CH}_2\text{CH}-$  of PS chain,  $-\text{C}(\text{CH}_3)_3$  and  $-\text{CH}_2\text{CH}-$  of PtBA), 2.08–2.47 ( $-\text{CH}_2\text{CH}-$  of PtBA), 3.09–3.55 ( $-\text{CHCH}_2\text{O}-$ ), 3.84–4.18 (m,  $-\text{CH}_2\text{COO}-$ ,  $-\text{OCH}_2\text{C}\equiv\text{CH}$ ), 6.30–7.30 (m,  $-\text{C}_6\text{H}_5$  of PS chain),  $M_n(\text{NMR}) = 5300$  g/mol. GPC:  $M_n(\text{GPC}) = 5500$  g/mol, PDI = 1.17. FTIR ( $\text{cm}^{-1}$ ): 3300 ( $-\text{C}\equiv\text{CH}$ ), 1737 ( $-\text{COO}-$ ).

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#### Preparation of Hyperbranched Polyglycerol with Multibromoisobutryl Groups (HPG-g-Br)

HPG 1.0 g [ $M_n(\text{NMR}) = 30,000$ , PDI = 1.27, 400 hydroxyl groups/HPG] was dried by azeotropic distillation with toluene and dissolved in 100 mL anhydrous pyridine, to which 3.4 mL (27 mmol) of 2-bromoisobutrylbromide was added dropwise at 0 °C over 30 min. The reaction was completed overnight. A large part of pyridine was distilled under reduced pressure with toluene; the residue was washed with cyclohexane and water three times to ensure all the impurities were moved out. After dried under vacuum at 45 °C for 12 h, transparent and viscous HPG-g-Br (2.30 g, 77.4% yield) with a pale yellow color was obtained. The percentage of esterification is 100%.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.93 (s,  $-\text{C}(\text{CH}_3)_2-\text{Br}$ ), 3.40–4.00 (m,  $\text{CH}$ ,  $\text{CH}_2$  of HPG), 4.18, 4.34, 4.50, 5.12, 5.25 (m,  $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}_2-$ ,  $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}-$ ). FTIR ( $\text{cm}^{-1}$ ): 1731 ( $-\text{COO}-$ ).

#### Preparation of Hyperbranched Polyglycerol with Multi azide Groups (HPG-g-N<sub>3</sub> (7))

The azidation of the bromide atom on HPG was proceeded as follows: 1.0 g [ $M_n(\text{NMR}) = 89,200$  g/mol, ~400 Br groups/HPG-g-Br, 4.48 mmol Br] HPG-g-Br was dissolved in 50 mL of DMF, then  $\text{NaN}_3$  (0.72 g, 11.1 mmol) was added and stirred for 48 h at room temperature. After the remove of salts by extraction, the product was precipitated in ethyl ether and dried under vacuum at 45 °C for 12 h until a constant weight (0.61 g, 73.5% yield) and stored at -20 °C for use.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.46 (s,  $-\text{C}(\text{CH}_3)_2-\text{N}_3$ ), 3.40–4.00 (m,  $\text{CH}$ ,  $\text{CH}_2$  of HPG), 4.18, 4.34, 4.50, 5.12, 5.25 (m,  $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}_2-$ ,  $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}-$ ). FTIR ( $\text{cm}^{-1}$ ): 2100 ( $-\text{N}_3$ ), 1731 ( $-\text{COO}-$ ), 1121 ( $-\text{C}-\text{O}-\text{C}-$ ).

#### Preparation of Star Graft Copolymers HPG-g-PS/PtBA (8)

Typically, in a 50 mL ampoule, 0.31 g PS-alkyne-PtBA [(5),  $M_n(\text{NMR}) = 5300$  g/mol, 0.058 mmol], 0.14 g HPG-g-N<sub>3</sub> [(7),  $M_n(\text{NMR}) = 74,000$  g/mol, ~400 Br groups/HPG-g-N<sub>3</sub>, 0.76 mmol N<sub>3</sub> groups], DMF (10 mL), CuBr (267 mg, 1.8 mmol), and PMDETA (311 mg, 1.8 mmol) were charged. The reaction mixture was then vacuumed by three freeze-thaw cycles and purged with N<sub>2</sub>, heated to 80 °C for 48 h. After the evaporation of DMF, the

reaction mixture was diluted with THF and passed through an activated basic alumina column to remove the copper salts. The crude product was diluted with methanol and small molecular compounds were removed by ultra filtration membrane. The final product HPG-*g*-PS/*Pt*BA was concentrated and dried under vacuum at 45 °C for 12 h until a constant weight (0.33 g, 71.7% yield) was obtained.

<sup>1</sup>H NMR (CDCl<sub>3</sub>) δ (ppm): 1.26–2.06 (m, –CH<sub>2</sub>CH– of PS chain, –C(CH<sub>3</sub>)<sub>3</sub> and –CH<sub>2</sub>CH– of *Pt*BA), 2.08–2.47 (–CH<sub>2</sub>CH– of *Pt*BA), 3.40–4.00 (m, CH, CH<sub>2</sub> of HPG), 6.30–7.30 (m, –C<sub>6</sub>H<sub>5</sub> of PS chain), *M*<sub>n</sub>(NMR) = 2.20 × 10<sup>5</sup> g/mol. GPC: *M*<sub>n</sub>(GPC) = 54,000 g/mol, PDI = 1.12, *M*<sub>w</sub>(GPC-MALLS) = 1.92 × 10<sup>5</sup> g/mol. FTIR (cm<sup>-1</sup>): 1121 (–C–O–C–), 1646 (–C=N–), 1737 (–COO–).

### Measurements

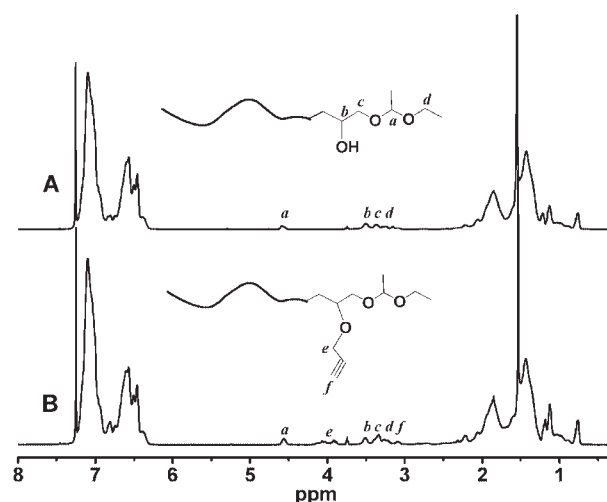
<sup>1</sup>H NMR measurements were carried out on a Bruker (500 MHz) NMR instrument, using CDCl<sub>3</sub> as the solvent and tetramethylsilane as the interior reference. The number-average molecular weight, *M*<sub>n</sub>, and PDI, *M*<sub>w</sub>/*M*<sub>n</sub>, were measured by GPC through three Waters Styragel columns (pore size 10<sup>2</sup>, 10<sup>3</sup>, and 10<sup>4</sup> Å) in series calibrated by narrow PS standard with molecular weight ranging from 2.20 × 10<sup>3</sup> to 5.15 × 10<sup>5</sup> g/mol. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. The elution of the sample was detected by a Waters 410 RI detector. GPC-MALLS-Viscosity-DRI analysis was performed using a Wyatt system equipped with a Water 515 pump, three ME-gel SD Plus columns (10<sup>3</sup>, 10<sup>5</sup>, 10<sup>6</sup> Å in series), DAWN HELEOS (14–154°) (Wyatt multiangle LS detector, He-Ne 658.0 nm), ViscoStar (Wyatt viscosity detector), and Optilab rEX (Wyatt RI detector). THF was used as eluent at a rate of 1 mL/min at 35 °C. The refractive index increment (dn/dc) was 0.144. Fourier transform infrared (FTIR) spectra were recorded on Magna 550 FTIR instrument. The polymer samples were dissolved in dry dichloromethane or methanol and then cast onto a NaCl disk to form the film by the evaporation of the solvent under infrared lamp. The Ultra Filtration Membrane Separator was purchased from Shanghai Institute of Applied Physics, Chinese Academy of Science, the cut-off molecular weight of used poly(ether sulfone) film: *M*<sub>w cut-off</sub> = 6000 g/mol (calibrated by globin).

## RESULTS AND DISCUSSION

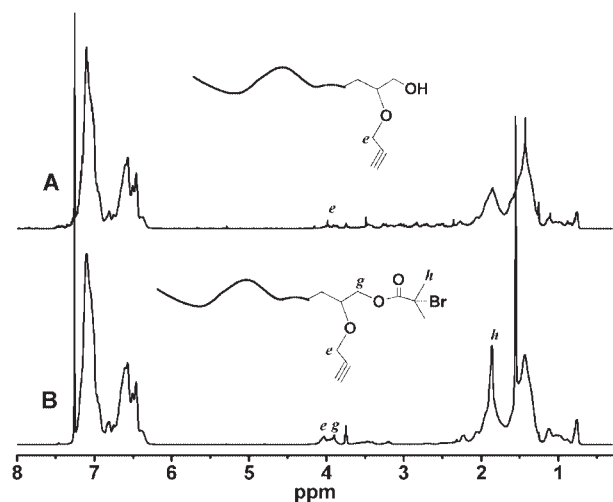
### Synthesis and Characterization of V-Shaped Copolymer PS-alkyne-*Pt*BA (5) with an Alkyne Group at the Conjunction Point

In a previous work,<sup>34</sup> the PS-EEGE [(1), *M*<sub>n</sub>(GPC) = 2300 g/mol, PDI = 1.04] with an active and a protected hydroxyl group at ω-end was synthesized by capping the poly(styryl)lithium (PS<sup>-</sup>Li<sup>+</sup>) with EEGE. The obtained PS-EEGE was used as the starting material and modified by the following procedure. First, the alkyne group was introduced to ω-end of PS-alkyne-EEGE by the reaction of propargyl bromide with the active hydroxyl group in DPMK/THF system at 0 °C. Then the ethoxyethyl group used as the protecting group was removed by hydrolysis in THF/HCl aqueous solution (37%) system and the recovered active hydroxyl group was modified by the reaction with 2-bromoisobutyryl bromide in pyridine at 0 °C. The transformation of functionalized PS-EEGE (1) to PS-alkyne-EEGE (2), PS-alkyne-OH (3) and PS-alkyne-Br (4) were all well-characterized by <sup>1</sup>H NMR in detail (Figs. 1 and 2) and the functionalization efficiency for each step was calculated (98.9, 100, 96.6%, respectively) (see the Supp. Info. for the detailed calculation).

In the transformation, the characteristic resonance signal for methylene group protons (–OCH<sub>2</sub>C≡CH) was detected at 3.84–4.18 ppm (e) in PS-alkyne-EEGE (2), the signal for methine group proton (–OCH(CH<sub>3</sub>)O–) at 4.65–4.76 ppm (a) in PS-alkyne-OH (3) disappeared completely after the hydrolysis of ethoxyethyl groups, and



**Figure 1.** <sup>1</sup>H NMR spectra of PS-EEGE (A) (1) and PS-alkyne-EEGE (B) (2), (solvent: CDCl<sub>3</sub>).

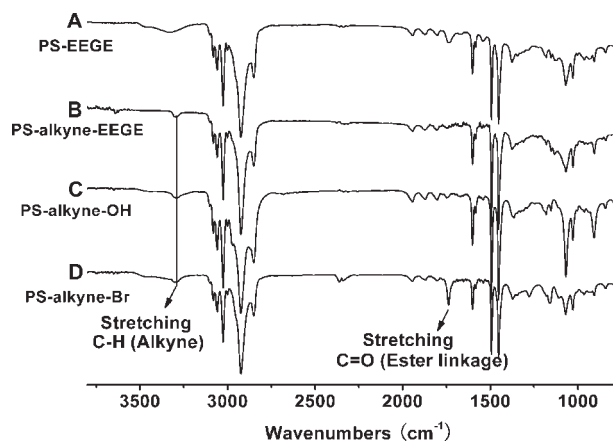


**Figure 2.**  $^1\text{H}$  NMR spectra of PS-alkyne-OH (A) (3) and PS-alkyne-Br (B) (4) (solvent:  $\text{CDCl}_3$ ).

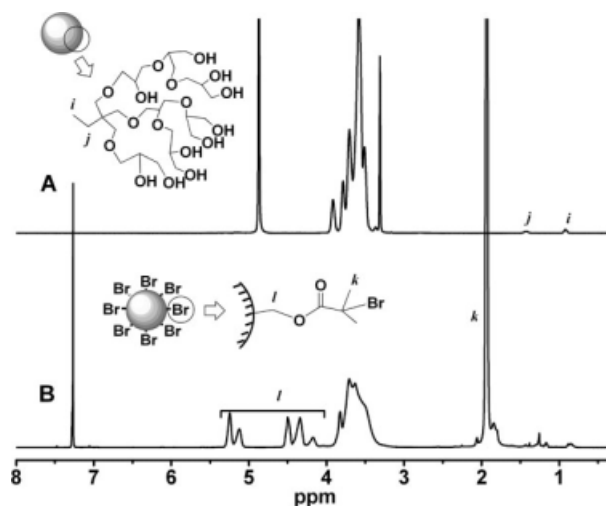
the signal for methylene group protons ( $-\text{CH}_2\text{COO}-$ ) at 3.84–4.18 ppm (g) in PS-alkyne-Br (4) was observed after the reaction of hydroxyl group of PS-alkyne-OH with 2-bromoisobutyryl bromide.

FTIR analysis showed (Fig. 3) that the alkyne group at  $3300\text{ cm}^{-1}$  for PS-alkyne-EEGE (2) and PS-alkyne-OH (3), and alkyne group at  $3300\text{ cm}^{-1}$  and ester bond at  $1737\text{ cm}^{-1}$  for PS-alkyne-Br (4) provided the further evidence for the successful transformation of the intermediates.

Using the PS-alkyne-Br (4) as macroinitiator, the  $\text{CuBr}/\text{PMDETA}$  as catalyst system and toluene as solvent, the V-shaped copolymer PS-



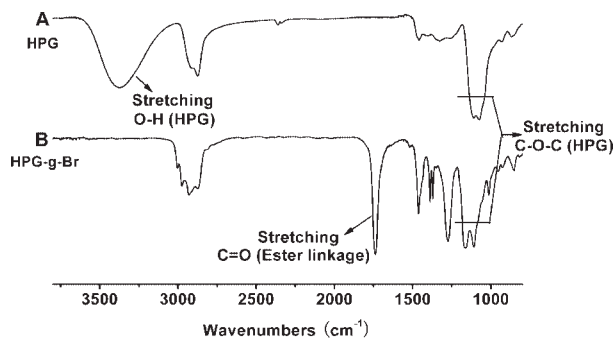
**Figure 3.** FTIR spectra of PS-EEGE (A) (1), PS-alkyne-EEGE (B) (2), PS-alkyne-OH (C) (3), and PS-alkyne-Br (D) (4).



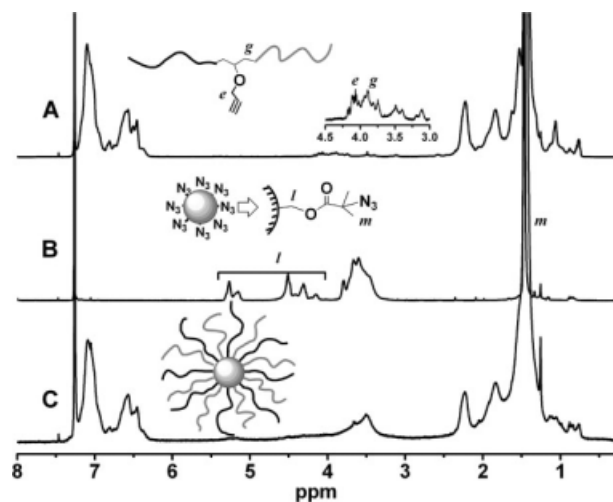
**Figure 4.**  $^1\text{H}$  NMR spectra of HPG (A) (solvent:  $\text{CD}_3\text{OD}$ ) and HPG-g-Br (B) (6) (solvent:  $\text{CDCl}_3$ ).

alkyne-*Pt*BA (5) with an alkyne group at the conjunction point was achieved by ATRP of *t*BA monomer at  $80\text{ }^\circ\text{C}$ . The uninitiated PS-alkyne-Br (4) accompanied in PS-alkyne-*Pt*BA could be separated by column chromatography, in which the PS-alkyne-Br (4) was first eluted by toluene and then the PS-alkyne-*Pt*BA copolymer eluted by THF completely. The monomodal GPC curves with a low PDI for the purified PS-alkyne-*Pt*BA (5) [ $M_n(\text{GPC}) = 5500\text{ g/mol}$ ,  $\text{PDI} = 1.17$ ] confirmed the effective separation procedure [Fig. 8(B)].

Figure 6(A) was the  $^1\text{H}$  NMR spectrum of purified PS-alkyne-*Pt*BA (5), besides the aromatic protons ( $-\text{C}_6\text{H}_5$ ) at 6.30–7.30 ppm for the PS chain, the methine group protons ( $-\text{CH}_2\text{CH}-$ ) at 2.08–2.42 ppm ascribed to the *Pt*BA chain were detected. However, the methyl group protons ( $-\text{CH}_3$ ) and the methylene group protons ( $-\text{CH}_2\text{CH}-$ ) at 1.20–2.01 ppm for *Pt*BA chain were overlapped by the protons ( $-\text{CH}_2\text{CH}-$ ) on



**Figure 5.** FTIR spectra of HPG (A), HPG-g-Br (B) (6).



**Figure 6.**  $^1\text{H}$  NMR spectra of PS-alkyne-*Pt*BA (A) (5), HPG-*g*- $\text{N}_3$  (B) (7), and HPG-*g*-PS/*Pt*BA (C) (8) (solvent:  $\text{CDCl}_3$ ).

PS chain. The characteristic resonance signal for methylene group protons ( $-\text{CH}_2\text{COO}-$ ) and methylene group protons ( $-\text{OCH}_2\text{C}\equiv\text{CH}$ ) at 3.84–4.18 ppm (g, e) proved the alkyne group was located at the conjunction point after polymerization of *t*BA. According to the already known  $M_n(\text{GPC})$  of PS-EEGE, the molecular weight  $M_n(\text{NMR})$  of PS-alkyne-*Pt*BA (5) could also be calculated from the NMR spectrum [ $M_n(\text{NMR}) = 5300 \text{ g/mol}$ ] (Table 1, see the Supp. Info. for the detailed calculation).

The typical FTIR spectrum of the V-shaped copolymer was shown in Figure 7(A). The presence of carbonate group ( $-\text{COO}-$ ) in the polymer backbone was supported by the strong absorption peak at  $1731 \text{ cm}^{-1}$ , and the two peaks at  $3020\text{--}3100 \text{ cm}^{-1}$  and  $3300 \text{ cm}^{-1}$  were ascribed to aro-

matic ( $-\text{C}-\text{H}$ ) and alkyne group ( $-\text{C}\equiv\text{C}-\text{H}$ ), respectively.

### Synthesis and Characterization of the HPG-*g*- $\text{N}_3$ Core Molecules (7)

Using the same method mentioned in our previous work,<sup>24</sup> the HPG-*g*-Br [ $M_n(\text{NMR}) = 89,200 \text{ g/mol}$  ( $\sim 400 \text{ Br groups/HPG-}g\text{-Br}$ , see the Supp. Info. for the detailed calculation)] was obtained after esterification of HPG.

Figure 4 was the  $^1\text{H}$  NMR spectra of HPG (A) and HPG-*g*-Br (B). Comparing with A of the HPG scaffold, the original five resonances observed in the range of 3.40–4.10 ppm for methylene and methine ( $\text{CH}$ ,  $\text{CH}_2$  of HPG scaffold) were moved to 4.10–5.50 ppm (l) ( $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}_2-$ ,  $\text{Br}-\text{C}(\text{CH}_3)_2-\text{COO}-\text{CH}-$ ) in B. The appearance of the resonances at 1.93 ppm (k) for the protons of the methyl groups close to Br atoms ( $-\text{C}(\text{CH}_3)_2-\text{Br}$ ) also proved the successful reaction. Thus, the degree of esterification (D.E.) can be obtained (see the Supp. Info. for the detailed calculation), the values of D.E.(1) and D.E.(2) are 100 and 97.5%, respectively. These results indicated all the hydroxyl groups on HPG were transformed into ester groups. FTIR analysis shown in Figure 5 provided another evidence for the esterification, the absorbance of characteristic ester group ( $-\text{COO}-$ ) at  $1731 \text{ cm}^{-1}$  appeared and the hydroxyl group ( $-\text{OH}$ ) at  $3400 \text{ cm}^{-1}$  disappeared.

The bromide atoms on HPG-*g*-Br were further quantitatively transformed into the azide groups by azidation with the  $\text{NaN}_3$  in DMF [ $M_n(\text{NMR}) = 74,000 \text{ g/mol}$ ,  $\sim 400 \text{ Br groups/HPG-}g\text{-N}_3$ , Table 1, see the Supp. Info. for the detailed calculation].

In the  $^1\text{H}$  NMR spectrum [Fig. 6(B)], the methyl group protons ( $-\text{C}(\text{CH}_3)_2-\text{N}_3$ ) derived

**Table 1.** Data of Star Graft Copolymers HPG-*g*-PS/*Pt*BA and Their Intermediates

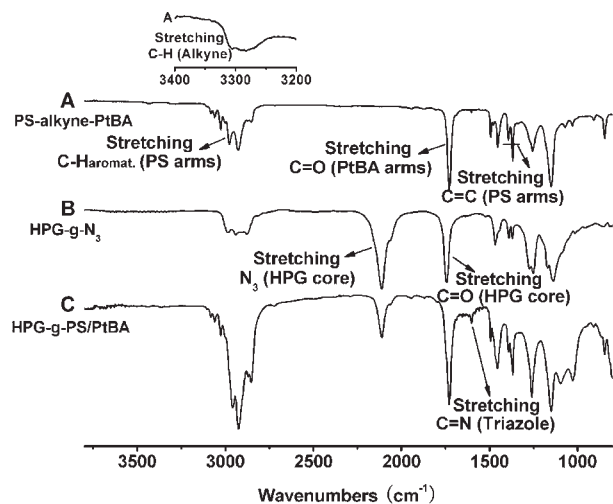
| Exp.                       | HPG- <i>g</i> -PS/ <i>Pt</i> BA |                              |                         |        |               |                    |               |                    |        |
|----------------------------|---------------------------------|------------------------------|-------------------------|--------|---------------|--------------------|---------------|--------------------|--------|
|                            | PS- <i>b</i> - <i>Pt</i> BA     | HPG- <i>g</i> - $\text{N}_3$ | Feed Ratio <sup>b</sup> | GPC    |               | $^1\text{H}$ NMR   |               | GPC-MALLS          |        |
| $M_n$ (g/mol) <sup>a</sup> | $M_n$ (g/mol) <sup>a</sup>      | $M_n$ (g/mol)                |                         | PDI    | $M_n$ (g/mol) | Ratio <sup>c</sup> | $M_w$ (g/mol) | Ratio <sup>d</sup> |        |
| S1                         | 5,300                           | 74,000                       | 30:1                    | 54,000 | 1.12          | 220,000            | 27.5:1        | 192,000            | 22.3:1 |
| S2                         | 5,300                           | 74,000                       | 50:1                    | 66,000 | 1.14          | 323,000            | 47.0:1        | 312,000            | 44.9:1 |

<sup>a</sup> Determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$ .

<sup>b</sup> Feed ratio represents the molar ratio of PS-alkyne-*Pt*BA and HPG-*g*- $\text{N}_3$  fed in the reactions.

<sup>c</sup> Represents the molar ratio of “V-shaped” side chains and HPG core calculated by  $^1\text{H}$  NMR (see the Supporting Information for the detailed calculation.).

<sup>d</sup> Represents the molar ratio of “V-shaped” side chains and HPG core calculated by GPC-MALLS, using the following formula:  $(M_w - 74,000)/5,300$ .



**Figure 7.** FTIR spectra of PS-alkyne-PtBA (A) (5), HPG-*g*-N<sub>3</sub> (B) (7), and HPG-*g*-PS/PtBA (C) (8).

from (—C(CH<sub>3</sub>)<sub>2</sub>—Br) [1.93 ppm (k)] was fully shifted to 1.46 ppm (m); and in FTIR spectrum [Fig. 7(B)], the absorbance of characteristic azide group (—N<sub>3</sub>) was observed at 2100 cm<sup>-1</sup>.

#### Synthesis and Characterization of Star Graft Copolymers HPG-*g*-PS/PtBA (8)

HPG-*g*-PS/PtBA was obtained by “click” chemistry between the alkyne groups [on PS-alkyne-PtBA (5)] and the azide groups [on HPG-*g*-N<sub>3</sub> (7)] under the CuBr/PMDETA system in DMF at 80 °C. After complete removal of copper salts by basic alumina column, the crude product was purified further by ultra filtration membrane with methanol as the solvent, which was an efficient method to remove the small molecules and also avoid the sample loss in the common precipitation.

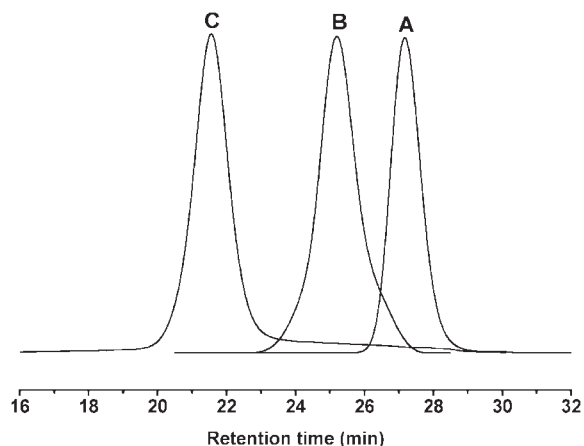
Figure 6(C) showed the <sup>1</sup>H NMR spectrum of HPG-*g*-PS/PtBA (8) in which three main regions can be observed. The resonances for the phenyl groups on PS occur in the region 6.30–7.30 ppm, methylene and methine groups on HPG in 3.40–5.50 ppm; separate resonances for methyl, methylene and methine groups on PS and PtBA are observed in 0.98–2.42 ppm which confirmed the successful synthesis of star graft copolymers.

Three main regions can also be observed in FTIR spectrum [Fig. 7(C)]: 1121 cm<sup>-1</sup> for —C—O—C— stretching on HPG core, 1727 cm<sup>-1</sup> for (—COO—) group on PtBA arms and 3020–3100 cm<sup>-1</sup> for (—C—H<sub>aromat</sub>) group on PS arms. Besides, 3300 cm<sup>-1</sup> for (—C≡CH) group on PS-alkyne-PtBA [Fig. 7(A)] completely disappeared, 2100 cm<sup>-1</sup> for (—N<sub>3</sub>) group on HPG-*g*-N<sub>3</sub> (7) [Fig.

7(B)] decreased and new peak at 1646 cm<sup>-1</sup> for (—C=N—) group on the star graft copolymers [Fig. 7(C)] can be detected.

It was observed that the *M<sub>n</sub>* of stars, estimated from GPC with linear PS standards, were smaller than the values theoretically predicted because of the smaller hydrodynamic volume of the star polymers than that of the linear chains, so the *M<sub>n</sub>* of HPG-*g*-PS/PtBA (8) obtained from GPC (S1: 54,000 g/mol, S2: 66,000 g/mol in Table 1) were unreliable. On the other hand, in the star polymers, the core were wrapped by the side chains, so the integration of the proton peak area of the core and part of the side chains close to the core in <sup>1</sup>H NMR were not very accurate. Thus, the protons from the core showed a weak and broad peak in the <sup>1</sup>H NMR spectrum due to the partial immobilization [Fig. 6(C)], and this deviation for the measurement of molecular weight was inevitable for the <sup>1</sup>H NMR analysis of star polymers. It means the *M<sub>n</sub>*(NMR) of S1 (220,000 g/mol) and S2 (323,000 g/mol) (Table 1, see the Supp. Info. for the detailed calculation) were also not very accurate. Here, GPC-MALLS was used to provide the weight-average molecular weight of the star graft copolymers, the values are 192,000 g/mol for S1 and 312,000 g/mol for S2 respectively (Table 1), both of them are approximate to the NMR values. Thus the average number of V-shaped side chains in each polymer could be calculated (S1: 22.3, S2: 44.9) which were very close to the feed ratio. It means that the coupling efficiency is much high.

It was found that when the molecular weight of V-shaped side chains was increased, the coupling efficiency would be dropped,<sup>35</sup> the further investigation is undergoing.



**Figure 8.** GPC curves of PS-EEGE (A) (1), PS-alkyne-PtBA (B) (5), and HPG-*g*-PS/PtBA (C) (8).



## CONCLUSIONS

The V-shaped side chains bearing a “clickable” alkyne group at the conjunction point of the two different PS and P $\epsilon$ BA blocks could be prepared by the combination of anion polymerization and ATRP. Then star graft copolymers were obtained by the click reaction of alkene group of the V-shaped side chains with azide groups on HPG core. This work provided a versatile and efficient route to synthesize graft copolymers with the V-shaped side chains.

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