

Synthesis of ABCD 4-Miktoarm Star-Shaped Quarterpolymers by Combination of the “Click” Chemistry with Multiple Polymerization Mechanism

GUOWEI WANG, XIAOLAN LUO, CHAO LIU, JUNLIAN HUANG

The Key Laboratory of Molecular Engineering of Polymers, State Education Ministry of China, Department of Macromolecular Science, Fudan University, Shanghai 200433, China

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ABSTRACT: Well-defined ABCD 4-Miktoarm star-shaped quarterpolymers of [poly(styrene)-poly(*tert*-butyl acrylate)-poly(ethylene oxide)-poly(isoprene)] [star(PS-*Pt*BA-PEO-PI)] were successfully synthesized by the combination of the “click” chemistry and multiple polymerization mechanism. First, the poly(styryl)lithium (PS⁻Li⁺) and the poly(isoprene)lithium (PI⁻Li⁺) were capped by ethoxyethyl glycidyl ether (EEGE) to form the PS and PI with both an active ω -hydroxyl group and an ω' -ethoxyethyl-protected hydroxyl group, respectively. After these two hydroxyl groups were selectively modified to propargyl and 2-bromoisobutyryl group for PS, the resulted PS was used as macroinitiator for ATRP of *t*BA monomer and the diblock copolymer PS-*b*-*Pt*BA with a propargyl group at the junction point was achieved. Then, using the functionalized PI as macroinitiator for ROP of EO monomer and bromoethane as blocking agent, the diblock copolymer PI-*b*-PEO with a protected hydroxyl group at the conjunction point was synthesized. After the hydrolysis, the recovered hydroxyl group of PI-*b*-PEO was modified to bromoacetyl and then azide group successively. Finally, the “click” chemistry between them was proceeded smoothly. The obtained star-shaped quarterpolymers and intermediates were characterized by ¹H NMR, FT-IR, and SEC in detail. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 2154–2166, 2008

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INTRODUCTION

Over the last few years, diverse polymer with complicated structures were synthesized and tailored for some specific properties, such as the comb-type,¹ hyperbranched,² cyclic,³ dendritic,⁴ and star-shaped copolymers.⁵ Specially, the asymmetric star copolymers were designed by

connecting several different chains into one point, which would be endowed with some promising properties and applications.⁶ The latest reports on the novel and more complex morphologies or self-assembly behavior derived from asymmetric stars copolymers had provoked the considerable interest of researchers.⁷ Thus, the exploration of new synthetic route to novel asymmetric star copolymers was the prerequisite.

Comparing with ABC 3-Miktoarm star-shaped copolymers, the synthesis of ABCD 4-Miktoarm showed the huger challenge because of its more complicated structure and the statistical

Correspondence to: J. Huang (E-mail: jlhuang@fudan.edu.cn)

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combination. Until recently, there were limited articles concerned the ABCD star-shaped copolymers. Originally, Iatrou and Hadjichristidis⁸ synthesized star[polystyrene(PS)-polybutadiene (Pbd)-polyisoprene(PI)-poly(4-methylstyrene) (P4MeS)] by the step-by-step titration method using SiCl₄ as the linking agent. In a recent work, they synthesized the star[PS-poly(dimethylsiloxane) (PDMS)-PI-poly(2-vinyl pyridine) (P2VP)]⁹ in the presence of 4-(dichloromethylsilyl) diphenylethylene (DCMSDPE) with two SiCl groups (linking agent) and a nonhomopolymerizable double bond (diphenylethylene). Hirao and coworkers¹⁰ designed a novel iterative methodology, which involves two steps for the reaction: (a) a coupling reaction of the benzyl bromide-functionalized polymer with a —CH₂OSiMe₂Bu^t diphenylethylene end-capped living chain and (b) a transformation of —CH₂OSiMe₂Bu^t to —CH₂Br. The star[PS-poly(methyl methacrylate) (PMMA)-poly(a-methylstyrene)(PaMeS)-P4MeS] copolymers were synthesized by repeating these two reactions. They also synthesized a series of ABCD star-shaped copolymers by developing another iterative methodology by the following reactions:^{11,12} (a) an addition reaction of living anionic polymer to 1,1-diphenylethylene (DPE)-functionalized polymer and (b) an *in situ* coupling reaction of the generated 1,1-diphenylalkyl anion with 1-(4-(3-bromopropyl)phenyl)-1-phenyl-ethylenes. By means of these methods, the coupling reaction could be carried out with the high efficiency, and the M_n of each segment could be well controlled even the M_n was more than 10,000 g/mol. However, a commonly encountered drawback for all these methods was that the polymerization must be carried out by the anionic polymerization technique and operated under the following conditions: (a) the high vacuum conditions and (b) the critical molar ratio between the added polymer precursors. On the other hand, the monomers suited for the anionic polymerization were limited. Thus, the single anionic polymerization was restricted in the preparation of copolymers with complicated structure.

Up to now, several other polymerization techniques had been explored, including the atom transfer radical polymerization (ATRP),¹³ nitroxide-mediated polymerization (NMP),¹⁴ and reversible addition fragmentation transfer polymerization (RAFT).¹⁵ And quite recently, the “click” chemistry as a novel way to construct polymer architecture has also been used extensively in polymer chemistry¹⁶ owing to its high

efficiency and technical simplicity.¹⁷ Usually, in the preparation of copolymers with complicated structure, a single method showed some limitations for the monomers available, and the strategy of combining several polymerization mechanism and linking methods would provide the possibility to construct more complicated structure and regulate the arrangement of different chains.¹⁸

In this presentation, a novel and universal route was suggested to synthesize the well-defined ABCD 4-Miktoarm star-shaped quarterpolymers of star(PS-*Pt*BA-PI-PEO). It was realized by the construction of diblock copolymers PS-*b*-*Pt*BA with a propargyl group and the PI-*b*-PEO with an azide group at the junction point first by the combination of living anionic polymerization, ATRP, and ROP mechanism, and then the “click” chemistry was successfully carried out between them. By means of this method, a variety of monomers could be used to prepare the ABCD 4-Miktoarm quarterpolymers, so, it would be possible to design the copolymers with the expected compositions.

EXPERIMENTAL

Materials

Styrene (St, >99.5%) was washed with 10% NaOH aqueous solution followed by water three times successively, dried over CaH₂, and distilled under reduced pressure. Ethylene oxide (EO) and isoprene were dried by CaH₂, and then distilled and stored at −20 °C before use. Glycidol (Tech., Acros), 1,1-diphenylmethane (99%), and *tert*-Butyl acrylate (*t*BA, Aldrich) were dried by CaH₂, and then distilled under reduced pressure and stored at −20°C before use. Bromoethane, *N,N*-dimethylformamide (DMF), toluene, cyclohexane, 1-butyl chloride, ethyl vinyl ether (98%, Aldrich), and propargyl bromide (>99%) were dried by CaH₂ and distilled just before use. Bromoacetyl bromide (>98%, Fluka), bromoisobutyryl bromide (98%, Aldrich), and *N,N,N',N'',N'''*-penta-methyl diethylenetriamine (PMDETA, Aldrich) were used as received. Tetrahydrofuran (THF, 99%) and pyridine (99.5%) were refluxed and distilled from sodium naphthalenide solution and sodium wire, respectively. Copper(I) bromide (CuBr, 95%) was stirred overnight in acetic acid, filtered, washed with ethanol and diethyl ether successively, and

dried *in vacuo*. Formic acid, sodium azide (NaN_3 , >98%), and potassium hydroxide (KOH) were all used as received. All other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., (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,¹⁹ the concentration was 0.61 mol/L. Ethoxyethyl glycidyl ether (EEGE) was synthesized from glycidol and ethyl vinyl ether according to Fitton et al.²⁰ and distilled under reduced pressure (b.p. 152–154 °C), and the purity exceeded 99.6 GC%.²¹ *n*-Butyllithium (*n*-BuLi) was prepared according to the literature²² and analyzed by the double-titration method²³ with the concentration of 1.57 mol/L.

Measurements

Size-exclusion chromatography (SEC) was performed in THF at 35 °C with an elution rate of 1.0 mL/min on an Agilent1100 with a G1310A pump, a G1362A refractive index detector, and a G1314A variable wavelength detector. One 5- μm LP gel column (500 Å, molecular range 500– 2×10^4 g/mol) and two 5- μm LP gel mixed bed column (molecular range 200– 3×10^6 g/mol) were calibrated by polystyrene standard samples. ^1H NMR spectra were obtained at a DMX500 MHz spectrometer with tetramethylsilane (TMS) as the internal standard and CDCl_3 as the solvent. Fourier transform infrared (FT-IR) spectra were recorded from 4000 to 400 cm^{-1} on a Magna-550 FT-IR instrument (NaCl tablet). The Ultra Filtration Separator was purchased from Shanghai Institute of Nuclear Research, Chinese Academy of Science, and the cutoff molecular weight of used poly(ether sulfone) membrane was calibrated by global protein.

Preparation of α -(*n*-Butyl)- ω -hydroxyl, ω' -Ethoxyethyl-poly(styrene) (PS(1)) and α -(*n*-Butyl)- ω -hydroxyl, ω' -Ethoxyethyl-poly(isoprene) (PI(2))

The “living” anionic polymerization of styrene and isoprene were carried out according to the literature²⁴ and the polystyrene (PS(1)) and polyisoprene (PI(2)) were characterized as follows.

PS(1): ^1H NMR (CDCl_3) δ ppm: 0.80(CH_3CH_2-), 1.13($\text{CH}_3\text{CH}_2\text{O}-$), 1.22($-\text{CH}(\text{CH}_3)-$), 1.26–2.01(m, 3H, aliphatic main chain $-\text{CH}_2\text{CH}-$

of PS), 3.09–3.43(m, $\text{CH}_3\text{CH}_2\text{O}-$, $-\text{CH}(\text{OH})\text{CH}_2\text{O}-$), 3.52($-\text{CH}(\text{OH})-$), 4.65–4.76 ($-\text{OCH}(\text{CH}_3)\text{O}-$), 6.30–7.30(m, 5H, aromatic $-\text{C}_6\text{H}_5$ of PS chain), $M_n(\text{NMR}) = 3100$ g/mol. SEC: $M_n(\text{SEC}) = 3000$ g/mol, PDI = 1.06. FT-IR (cm^{-1}): 1600, 1582, 1492, 1452(aromatic $-\text{C}-\text{C}-$).

PI(2): ^1H NMR (CDCl_3) δ ppm: 0.80 (CH_3CH_2-), 1.13($\text{CH}_3\text{CH}_2\text{O}-$), 1.22 (m, $-\text{CH}(\text{CH}_3)-$), 1.26–2.25 (m, $-\text{C}(\text{CH}_3)-$ and aliphatic main chain $-\text{CH}_2\text{CH}-$ of PI), 1.86 (m, $-\text{C}(\text{CH}_3)=\text{CH}-$, $-\text{C}(\text{CH}_3)=\text{CH}_2$), 3.09–3.43 (m, $\text{CH}_3\text{CH}_2\text{O}-$, $-\text{CH}(\text{OH})\text{CH}_2\text{O}-$), 3.52 ($-\text{CH}(\text{OH})-$), 4.65–4.76 ($-\text{OCH}(\text{CH}_3)\text{O}-$), 4.63–4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3, 4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.08 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition). SEC: $M_n(\text{SEC}) = 2200$ g/mol, PDI = 1.08. FT-IR (cm^{-1}): 3070 ($=\text{C}-\text{H}$), 1642($-\text{C}=\text{C}-$), 886($=\text{CH}_2$).

Preparation of α -(*n*-Butyl)- ω -propargyl, ω' -Ethoxyethyl-poly(styrene) (PS(3)) and α -(*n*-Butyl)- ω -propargyl, ω' -Hydroxyl-poly(styrene) (PS(4))

In a 250-mL dried ampoule, 10.0 g dried PS(1) ($M_n(\text{SEC})(1) = 3000$ g/mol, 3.33 mmol) and 150 mL THF were added. Then, the system was charged with 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(3) 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 (9.72 g, 97.2% yield) was obtained.

^1H NMR (CDCl_3) δ (ppm): 0.80(CH_3CH_2-), 1.13($\text{CH}_3\text{CH}_2\text{O}-$), 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 ($-\text{OCH}_2\text{C}\equiv\text{CH}$), 4.65–4.76 ($-\text{OCH}(\text{CH}_3)\text{O}-$). FT-IR (cm^{-1}): 3300($-\text{C}\equiv\text{CH}$).

The hydroxyl group was recovered by hydrolysis of ethoxyethyl group at ω end of PS(3). Typically, 9.0 g ($M_n(\text{SEC})(1) = 3000$ g/mol, 3.00 mmol) PS(3) was dissolved in 150 mL THF, and then 13 mL HCL(37%) was added and stirred for 2h at room temperature. The PS(4) 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 (8.52 g, 94.7% yield) was obtained.

^1H NMR (CDCl_3) δ (ppm): 0.80 (CH_3CH_2-), 3.09–3.55 ($-\text{CHCH}_2\text{OH}$), 3.84–4.18 ($-\text{OCH}_2\text{C}\equiv\text{CH}$). FT-IR (cm^{-1}): 3300($-\text{C}\equiv\text{CH}$).

Preparation of α -(*n*-Butyl)- ω -propargyl, ω' -(2-Bromoisobutyl)-poly(styrene) (PS(5))

In a 250-mL round bottom flask, 8.0 g ($M_{\text{n(SEC)(1)}} = 3000$ g/mol, 2.66 mmol) dried **PS(4)** was added and dissolved in 100 mL anhydrous pyridine. The system was placed in ice bath and 1.3 mL (10.5 mmol) 2-bromoisobutyl 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(5)** was obtained with the constant weight (7.42 g, 92.8% yield).

^1H NMR (CDCl_3) δ (ppm): 0.80 (CH_3CH_2-), 1.94 ($-\text{C}(\text{CH}_3)\text{Br}$), 3.09–3.55 ($-\text{CHCH}_2\text{O}-$), 3.84–4.18 (m, $-\text{CH}_2\text{COO}-$, $-\text{OCH}_2\text{C}\equiv\text{CH}$). FT-IR (cm^{-1}): 3304($-\text{C}\equiv\text{CH}$), 1737($-\text{COO}-$).

Preparation of Diblock Copolymer Poly(styrene)-*b*-poly(*tert*-butyl acrylate) (PS-*b*-PtBA (6))

The diblock copolymer of **PS-*b*-PtBA (6)** with a propargyl group at the conjunction point was carried out using **PS(5)** as macroinitiator, and the typical 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(5)** 3.0 g ($M_{\text{n(SEC)(1)}} = 3000$ 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, and 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/ H_2O system. After filtration, the products of **PS-*b*-PtBA (6)** were dried at 45 °C for 12 h until a constant weight (5.70 g, 84.9% yield) was obtained.

^1H NMR (CDCl_3) δ (ppm): 0.80 (CH_3CH_2-), 0.91–1.20 (m, $-\text{C}(\text{CH}_3)_2-$, CH_3- (CH_2)₃-), 1.26–2.06 (m, 3H, aliphatic main chain $-\text{CH}_2\text{CH}-$ of PS, $-\text{C}(\text{CH}_3)_3$ and $-\text{CH}_2\text{CH}-$ of PtBA), 2.08–2.47 ($-\text{CH}_2\text{CH}-$ of PtBA), 2.59 ($-\text{CH}_2\text{CH}(\text{Br})-$), 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, 5H, aromatic $-\text{C}_6\text{H}_5$ of PS chain), $M_{\text{n(NMR)}} = 8900$ g/mol. SEC: $M_{\text{n(SEC)}} = 8100$ g/mol, PDI = 1.17. FT-IR (cm^{-1}): 3300($-\text{C}\equiv\text{CH}$), 1728($-\text{COO}-$).

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Preparation of Diblock Copolymer PI-*b*-PEO(7) with an Ethoxyethyl-Protected Hydroxyl Group and PI-*b*-PEO(8) with an “Active” Hydroxyl Group at the Junction Point

The preparation procedure of diblock copolymers **PI-*b*-PEO(7)** was similar to that of **PS-*b*-PEO** in literature.²⁴

PI-*b*-PEO(7) with a protected hydroxyl group at the junction point: ^1H NMR (CDCl_3) δ (ppm): 0.80 (CH_3CH_2-), 1.13($\text{CH}_3\text{CH}_2\text{O}-$), 1.22 (m, $-\text{CH}(\text{CH}_3)-$), 1.26–2.25 (m, $-\text{C}(\text{CH}_3)-$ and aliphatic main chain $-\text{CH}_2\text{CH}-$ of PI), 1.86 (m, $-\text{C}(\text{CH}_3)=\text{CH}-$, $-\text{C}(\text{CH}_3)=\text{CH}_2$), 3.09–3.43 (m, $\text{CH}_3\text{CH}_2\text{O}-$, $-\text{CH}(\text{OH})\text{CH}_2\text{O}-$), 3.52 ($-\text{CH}(\text{OH})-$), 3.53–3.70 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO block), 4.65–4.76 ($-\text{OCH}(\text{CH}_3)\text{O}-$), 4.63–4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.08 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), $M_{\text{n(NMR)}} = 5800$ g/mol. SEC: $M_{\text{n(SEC)}} = 4500$ g/mol, PDI = 1.13. FT-IR (cm^{-1}): 3070($=\text{C}-\text{H}$), 1642($-\text{C}=\text{C}-$), 1121 ($-\text{C}-\text{O}-\text{C}-$), 886($=\text{CH}_2$).

PI-*b*-PEO(8) with an “active” hydroxyl group at the junction point: ^1H NMR (CDCl_3) δ (ppm): 0.80 (CH_3CH_2-), 3.09–3.53 ($-\text{CH}(\text{O}-)\text{CH}_2\text{O}-$), 3.53–3.70 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO block), 4.63–4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.08 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition). FT-IR (cm^{-1}): 3070($=\text{C}-\text{H}$), 1642($-\text{C}-\text{C}-$), 1121($-\text{C}-\text{O}-\text{C}-$), 886($=\text{CH}_2$).

Preparation of Diblock Copolymer PI-*b*-PEO(9) with a Bromide Atom at the Junction Point

In a 250-mL round bottom flask, 8.0 g (1.78 mmol) dried **PI-*b*-PEO(8)** was added dissolved in 100 mL anhydrous pyridine. The system was placed in ice bath and 1.2 mL (13.8 mmol) bromoacetyl bromide was added dropwise for 0.5 h. After the solution was stirred for 24 h, the pyridine was evaporated. The formed salts and small molecular compounds were removed by ultra filtration membrane, then the filtrate was distilled to dryness, and the product was precipitated in ethyl ether, filtrated, and dried under vacuum at 25 °C for 2 h until a constant weight (6.9 g, 86.3% yield) and the **PI-*b*-PEO(8)** was obtained.

^1H NMR (CDCl_3) δ (ppm): 0.80 (CH_3CH_2-), 4.05–4.46 ($-\text{COOCH}_2-$, BrCH_2-), 4.63–4.69

($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.08 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition). FT-IR (cm^{-1}): 3070($=\text{C}-\text{H}$), 1730($-\text{COO}-$), 1642($-\text{C}=\text{C}-$), 1121($-\text{C}-\text{O}-\text{C}-$), 886($=\text{CH}_2$).

Preparation of Diblock Copolymer PI-*b*-PEO(10) with an Azide Group Atom at the Junction point

The azidation of the bromide atom on **PI-*b*-PEO(9)** was proceeded as follows: Typically, 5.0 g (1.11 mmol) **PI-*b*-PEO(9)** was dissolved in 50 mL of DMF, then NaN_3 (0.36 g, 5.53 mmol) was added and stirred for 48 h at room temperature. After the removal of salts, the copolymer was precipitated in ethyl ether. The copolymer **PI-*b*-PEO(10)** was dried under vacuum at 25 °C for 2 h until a constant weight (4.5 g, 90.0% yield) was obtained and stored at -20 °C for use.

^1H NMR (CDCl_3) δ (ppm): 0.80 (CH_3CH_2-), 4.05–4.46 ($-\text{COOCH}_2-$), 4.63–4.69 ($-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.08 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition). FT-IR (cm^{-1}): 3070($=\text{C}-\text{H}$), 2100($-\text{N}_3$), 1730 ($-\text{COO}-$), 1642($-\text{C}=\text{C}-$), 1121($-\text{C}-\text{O}-\text{C}-$), 886($=\text{CH}_2$).

Preparation of 4-Miktoarm ABCD Quarterpolymer Star(PS-*Pt*BA-PEO-PI)(11)

Typically, in a 50-mL ampoule, 0.32 g **PS-*b*-*Pt*BA (6)** (4.9×10^{-5} mol, $M_{\text{n(SEC)}} = 6500$ g/mol, 1.0 equiv), 0.40 g **PI-*b*-PEO(10)** (8.9×10^{-5} mol, $M_{\text{n(SEC)}} = 4500$ g/mol, 1.6 equiv of $-\text{N}_3$ group), DMF (5 mL), CuBr (288.8 mg, 1.6×10^{-3} mol, 32 equiv), and PMDETA (276.8 mg, 1.6×10^{-3} mol, 32 equiv) were charged. The reaction mixture was then vacuumed by three freeze-thaw cycles and purged with N_2 , and then 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 resulting mixture was concentrated and dried under vacuum at 45 °C for 12 h until a constant weight (0.69 g, 95.2% yield based on the added diblock copolymers) was obtained. To remove the excess diblock copolymer of **PI-*b*-PEO(10)**, the above product was washed with the mixture of methanol/water and 0.51 g 4-Miktoarm ABCD quarterpolymer was obtained.

^1H NMR (CDCl_3) δ (ppm): 0.80 (m, CH_3CH_2-), 0.91–1.20 (m, 3H, aliphatic main chain $-\text{CH}_2\text{CH}-$ of PS, $-\text{C}(\text{CH}_3)_2-$, CH_3- (CH_2) $_3-$), 1.26–2.06 (m, 3H, aliphatic main chain $-\text{CH}_2\text{CH}-$ of PtBA, $-\text{C}(\text{CH}_3)_3$ and $-\text{CH}_2\text{CH}-$ of PtBA, $-\text{C}(\text{CH}_3)=\text{CH}-$, $-\text{C}(\text{CH}_3)=\text{CH}_2$) of PI), 2.08–2.47 (m, 4H, $-\text{CH}_2\text{CH}_2\text{O}-$ of PEO block), 4.63–4.69 (m, 4H, $-(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition), 4.95 ($-\text{CH}=\text{CH}_2$ of 1,2-addition), 5.08 ($-\text{CH}=\text{C}(\text{CH}_3)-$ of 1,4-addition), 5.70 ($-\text{CH}=\text{CH}_2$ of 1,2-addition) 6.30–7.30 (m, 5H, aromatic $-\text{C}_6\text{H}_5$ of PS chain), $M_{\text{n(NMR)}} = 11,900$ g/mol. SEC: $M_{\text{n(SEC)}} = 9300$ g/mol, PDI = 1.25. FT-IR (cm^{-1}): 1735($-\text{COO}-$).

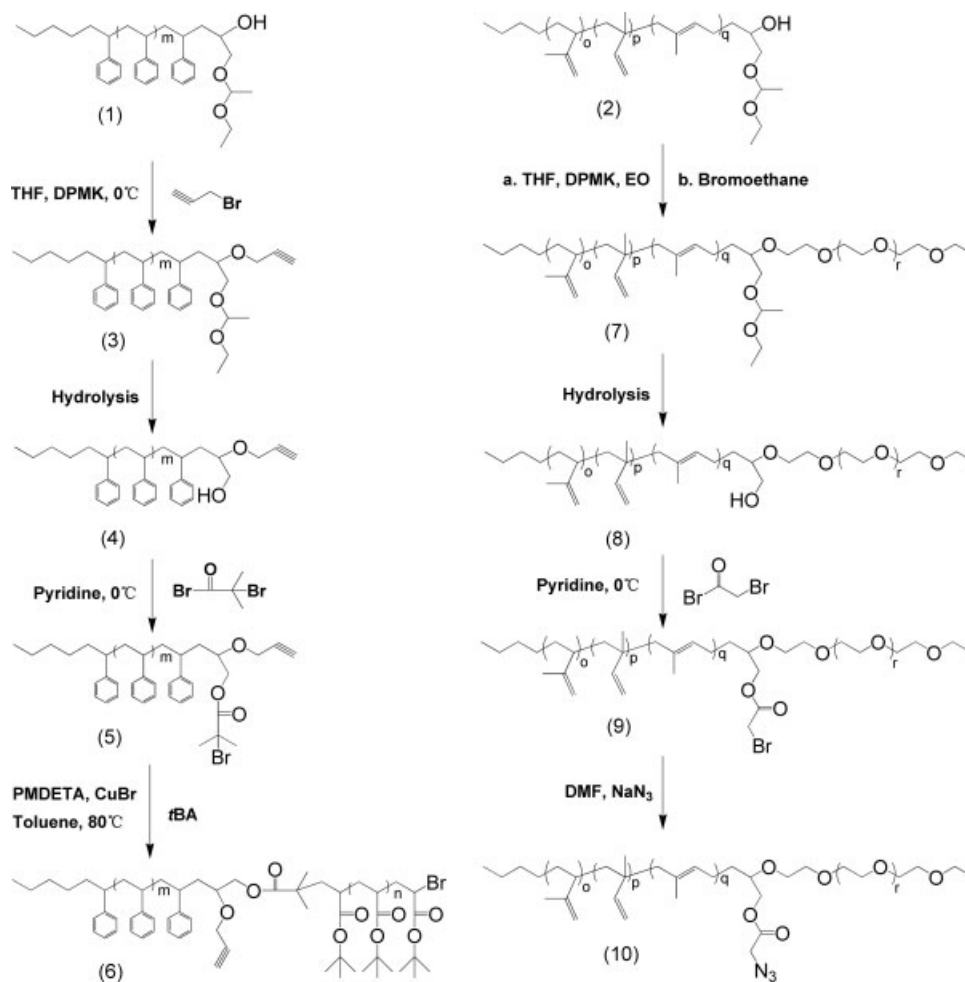
RESULTS AND DISCUSSION

In this contribution, the diblock copolymers of A-*b*-B with a propargyl group and C-*b*-D with an azide group at the junction point were prepared first, and then the “click” chemistry was proceeded between them (Scheme 1). Herein, the A, B, C, D represented poly(styrene) (PS), poly(*tert*-butyl acrylate) (*Pt*BA), poly(ethylene oxide) (PEO), and poly(isoprene) (PI), respectively.

Synthesis and Characterization of the Diblock Copolymer PS-*b*-*Pt*BA with a Propargyl Group at the Junction Point

In a previous work,²⁴ the **PS(1)** with an active and a protected hydroxyl group at ω -end was synthesized by capping the poly(styryl) lithium (PS^-Li^+) with ethoxyethyl glycidyl ether (EEGE). Herein, the **PS(1)** was used as the start material and modified by the following procedure. First, the propargyl group was introduced to ω -end of **PS(3)** by the reaction of propargyl bromide with the active hydroxyl group in diphenylmethyl potassium (DPMK)/THF system at 0 °C (Scheme 1). The ethoxyethyl group as the protecting group could be removed by hydrolysis in THF/HCl aqueous solution (37%) system and then the recovered active hydroxyl group was modified by the reaction with bromoisobutyryl bromide in pyridine at 0 °C. The transformation of functionalized **PS(1)** to **PS(3)**, **PS(4)**, and **PS(5)** were all well characterized by ^1H NMR in detail and calculated with the high E.F. (efficiency of functionalization) values (Figs. 1 and 2, Table 1).

In the transformation, the characteristic resonance signal for methylene group protons ($-\text{OCH}_2\text{C}\equiv\text{CH}$) was detected at 3.84–4.18 ppm



Scheme 1. Synthesis of diblock copolymer **PS-*b*-PtBA** with a propargyl group and **PI-*b*-PEO** with an azide group at the junction point.

in **PS(3)**, the signal for methine group proton ($-\text{OCH}(\text{CH}_3)\text{O}-$) at 4.65–4.76 ppm in **PS(4)** disappeared completely after the hydrolysis of

protected-hydroxyl group of **PS(3)**, and the signal for methylene group protons ($-\text{CH}_2\text{COO}-$) at 3.84–4.18 ppm in **PS(5)** was observed after

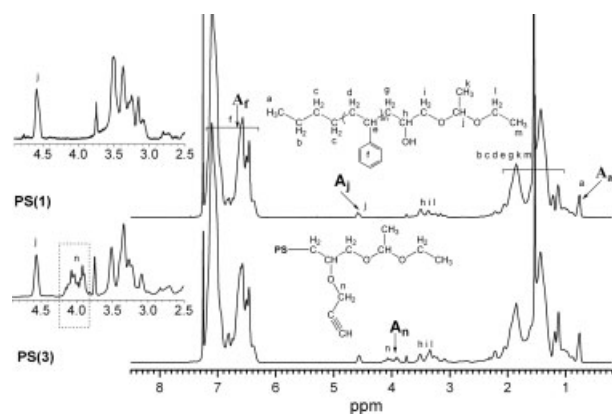


Figure 1. ^1H NMR spectra (CDCl_3) of **PS(1)** and **PS(3)**.

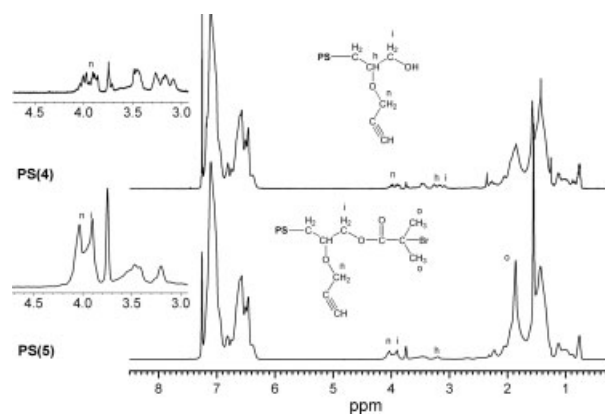


Figure 2. ^1H NMR spectra (CDCl_3) of **PS(4)** and **PS(5)**.

Table 1. The Polymerization Data of Diblock Copolymers **PS-*b*-PtBA** and Their Precursors of **PS**

Exp.	PS(1)		Efficiency of Functionalization (E.F.) (%)					PS- <i>b</i> -PtBA(6)				
	$M_{n(\text{SEC})}^a$ (g/mol)	PDI ^a	$M_{n(\text{NMR})}^b$ (g/mol)	N_s^c	E.F.(1) ^d	E.F.(3) ^e	E.F.(4) ^f	E.F.(5) ^g	$M_{n(\text{SEC})}^a$ (g/mol)	PDI ^a	$M_{n(\text{NMR})}^h$ (g/mol)	$N_{t\text{BA}}^c$
(6A)	3000	1.06	3100	30	97.3	99.2	100	97.3	8100	1.17	8900	45
(6B)	2300	1.06	2300	22	96.9	98.9	100	96.6	6500	1.13	6700	34
(6C)	4700	1.05	4900	47	98.6	99.7	100	98.6	14,300	1.23	15,400	82
(6D)	6200	1.04	6500	63	98.2	99.5	100	97.9	8700	1.06	9100	20

^a Determined by SEC with THF as solvent using PS standards.

^b $M_{n(\text{NMR})}$ was determined by ¹H NMR in CDCl₃ through the end group analysis based on the integral area using the formula: $M_{n(\text{NMR})\text{PS}(1)} = [(3 \times 104 \times A_f)/(5 \times A_a)] + 57 + 147$, where the A_f and A_a were the integral area of the aromatic protons ($-C_6H_5$) on PS chain at 6.30–7.30 ppm (f) and the characteristic α -methyl group protons ($-CH_3$) of the initiator (*n*-BuLi) residue at 0.80 ppm (a), respectively. The value 104 and 57 were the molecular weight of St unit and the mass of the α -end initiator residue butyl group ($-C_4H_9$). The value 147 was the sum between the mass of capping molecule EEGE ($C_7H_{14}O_3$) and that of a proton ($-H$) (see Fig. 1).

^c N_s and $N_{t\text{BA}}$ represent the monomer units on **PS(1)** and PtBA chains according to $M_{n(\text{SEC})}$, $M_{n(\text{NMR})}$, respectively.

^d E. F. (Efficiency of Functionalization) was determined by ¹H NMR in CDCl₃ using the formula: $\text{E.F.}(1) = [(3 \times A_j)/A_a] \times 100\%$, where the A_j was the integral area of *o*'-ethoxyethyl group proton ($-OCH(CH_3)O-$) at 4.65–4.76 ppm (j) (see Fig. 1).

^e E.F.(3) was calculated from the formula: $\text{E.F.}(3) = [A_n/(2 \times A_j)] \times 100\%$, where the A_n was the integral area of methylene group protons ($-OCH_2C\equiv CH$) at 3.84–4.18 ppm (n) (see Fig. 1).

^f E.F.(4) was calculated according to the completeness of hydrolysis for the acetal group at the end of **PS(3)** (see Fig. 2).

^g E.F.(5) was calculated according to the formula: $\text{E.F.}(5) = [(3 \times A_{n,p})/(4 \times A_a \times \text{E.F.}(1))] \times 100\% - \text{E.F.}(3)$, where the $A_{n,p}$ was the integral area of methylene group protons ($-OCH_2C\equiv CH$, $-COOCH_2-$) at 3.84–4.18 ppm (n,p) (see Fig. 2).

^h $M_{n(\text{NMR})}$ was determined by ¹H NMR in CDCl₃ according to the formula: $M_{n(\text{NMR})\text{PS-}b\text{-PtBA}(6)} = [(5 \times A_s \times M_{n(\text{SEC})\text{PS}(1)} + 128)/(A_f \times 104)] + M_{n(\text{SEC})\text{PS}(1)}$. The value of 128 was the molecular weight of *t*BA unit (see Fig. 4).

the reaction of hydroxyl group of **PS(4)** with 2-bromoisobutyryl bromide.

Using the **PS(5)** as macroinitiator, the CuBr/PMDETA as catalyst system, and toluene as solvent at 80 °C, the diblock copolymer **PS-*b*-PtBA(6)** with a propargyl group at the junction point was achieved by ATRP of *t*BA monomer. As the SEC curve in Figure 3 showed, there was uninitiated homopolymer PS accompanied in **PS-*b*-PtBA(6)**, and the former could be separated by column chromatography, in which the PS homopolymer was firstly eluted by toluene and then the **PS-*b*-PtBA(6)** diblock copolymer eluted by THF completely. The monomodal SEC curves with a low PDI for the purified **PS-*b*-PtBA(6)** confirmed the effective separation procedure.

Figure 4 was the ¹H NMR spectrum of purified **PS-*b*-PtBA(6)**, besides the aromatic protons ($-C_6H_5$) at 6.30–7.30 ppm for the PS chain, the methine group protons ($-CH_2CH-$) at 2.08–2.42 ppm (s) ascribed to the PtBA chain were detected. However, the methyl group protons ($-CH_3$) and the methylene group protons ($-CH_2CH-$) at 1.20–2.01 ppm for PtBA chain were overlapped by the protons ($-CH_2CH-$) on PS chain. According to the already known $M_{n(\text{SEC})\text{PS}(1)}$, the molecular weight $M_{n(\text{NMR})}$ of **PS-*b*-PtBA(6)** could be calculated (Table 1).

Synthesis of Diblock Copolymer **PI-*b*-PEO** and the Modification of Functional Groups at the Junction Point

As the capping reaction for **PS(1)**,²⁴ the poly(isoprene) (**PI(2)**) was also synthesized by the capping

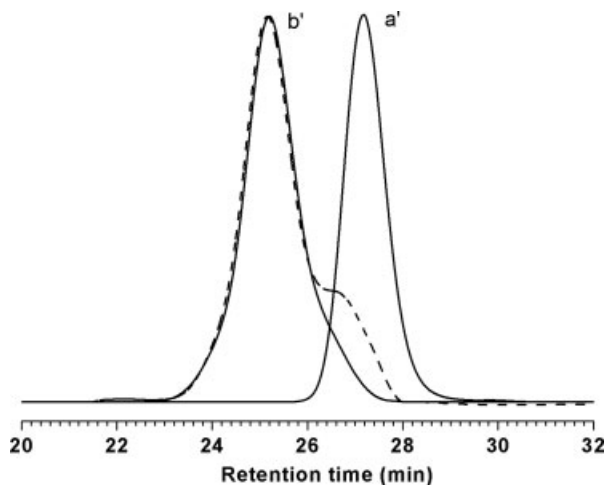


Figure 3. SEC curves of diblock copolymer **PS-*b*-PtBA(6)** (a', $M_{n(\text{SEC})} = 6500$) and its precursor **PS(1)** (b', $M_{n(\text{SEC})} = 2300$) (dot line: the copolymer before purification; solid line: the copolymer after purification).

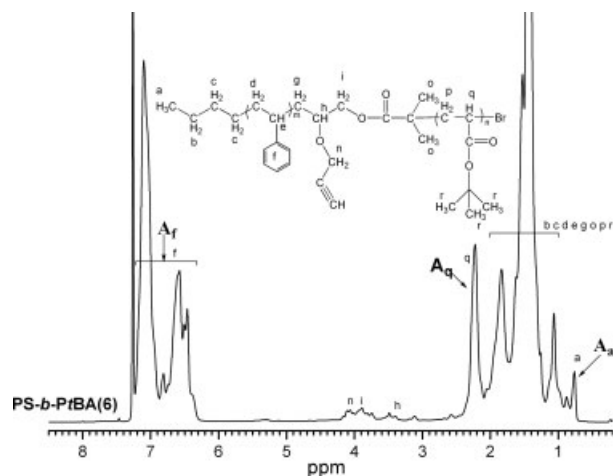


Figure 4. ^1H NMR spectrum (CDCl_3) of diblock copolymer **PS-*b*-PtBA(6)**.

of poly(isoprenyl)lithium (PI^-Li^+) with EEGE. The ^1H NMR (Fig. 5) spectrum confirmed the successful introduction of EEGE to PI end and the microstructure on PI chain: the signal at 5.70 ppm (c) was ascribed to the methine group protons ($-\text{CH}=\text{CH}_2$) for the 1,2-addition, the signal at 5.08 ppm (e) was ascribed to the methine group protons ($-\text{CH}=\text{C}(\text{CH}_3)$) for the 1,4-addition, the signal at 4.65–4.76 ppm was ascribed to the methylene group protons ($-\text{CH}=\text{CH}_2$) for 1,2-addition, and ($-\text{C}(\text{CH}_3)=\text{CH}_2$) for 3,4-addition.

Then, the **PI(2)** was used as macroinitiator for ROP of EO monomer in THF using DPMK as protonation agent. After the ROP of EO, the PEO species were blocked by bromoethane and the **PI-*b*-PEO(7)** with a protected group at the

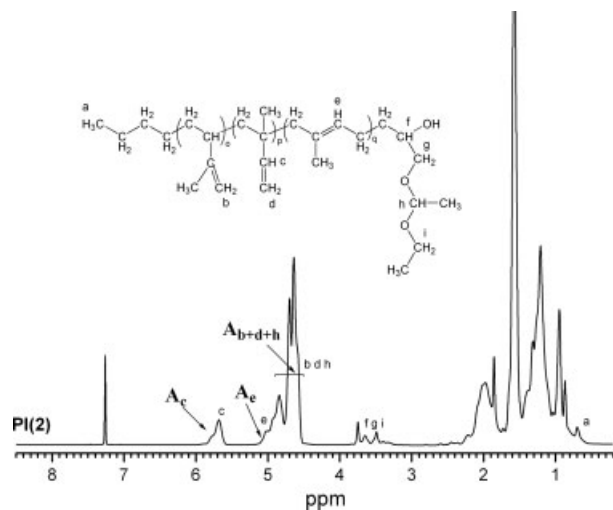


Figure 5. ^1H NMR spectrum (CDCl_3) of **PI(2)**.

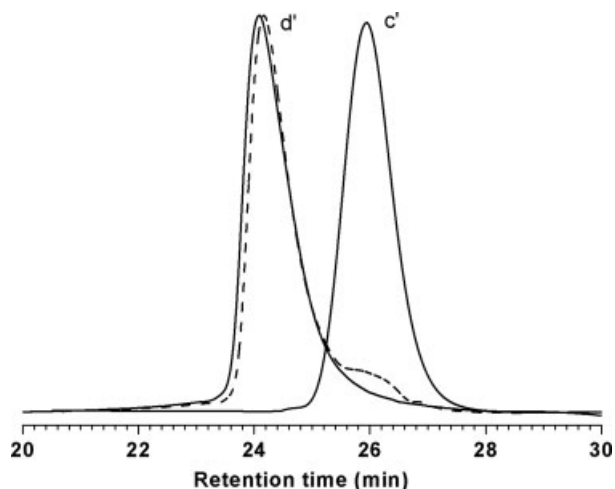


Figure 6. SEC curves of diblock copolymer of **PI-*b*-PEO(7)** (c' , $M_{n(\text{SEC})} = 10,900$) and its precursor **PI(2)** (d' , $M_{n(\text{SEC})} = 4500$) (dot line: the copolymer before purification; solid line: the copolymer after purification).

junction point was achieved, in which the procedure was similar to the previous preparation of **PS-*b*-PEO**.²⁴ There was some uninitiated **PI(2)** homopolymer coexisted in **PI-*b*-PEO(7)** and they could be separated by extraction with cyclohexane. From the SEC results (Fig. 6), the solid line with a monomodal for **PI-*b*-PEO(7)** proved the successful purification.

From ^1H NMR spectrum, the signal at 3.53–3.70 ppm (j) corresponding to the methylene group protons ($-\text{CH}_2\text{CH}_2\text{O}-$) confirmed the successful synthesis of **PI-*b*-PEO(7)** (Fig. 7). By

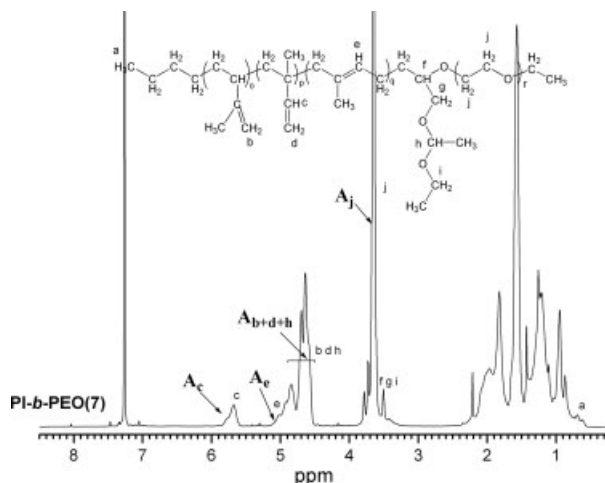


Figure 7. ^1H NMR spectrum (CDCl_3) of diblock copolymer **PI-*b*-PEO(7)**.

Table 2. Polymerization Data of **PI(2)** and the Diblock Copolymer **PI-*b*-PEO(7)**

Exp	PI(2)			PI-<i>b</i>-PEO(7)				E.F. (%)
	$M_{n(\text{SEC})}^a$ (g/mol)	PDI ^a	N_I ^b	$M_{n(\text{SEC})}^a$ (g/mol)	PDI ^a	$M_{n(\text{NMR})}^c$ (g/mol)	N_{EO} ^b	E.F.(9) ^d
(10)A	2200	1.08	32	4500	1.13	5800	82	89.6
(10)B	3100	1.07	46	6400	1.09	7200	93	85.7
(10)C	4500	1.06	66	10,900	1.05	12,000	170	91.2

^a Determined by SEC with THF as solvent using PS standards.

^b N_I , N_{EO} represent the monomer units on PI and PEO chains according to $M_{n(\text{SEC})}$, $M_{n(\text{NMR})}$, respectively.

^c $M_{n(\text{NMR})}$ of **PI-*b*-PEO(7)** was determined by ¹H NMR in CDCl₃ using the known $M_{n(\text{SEC})}$ of **PI(2)**.

^d E.F.(9) was calculated from ¹H NMR.

analyzing the integral area in ¹H NMR, the $M_{n(\text{NMR})}$ of **PI-*b*-PEO(7)** was determined by using the known $M_{n(\text{SEC})}$ of **PI(1)** (Table 2).

The ethoxyethyl group was removed by acidolysis with formic acid and the subsequent saponification with the KOH solution, which had been proved an efficient procedure for the removal of ethoxyethyl group in other works.²⁵ The recovered hydroxyl group at the junction point of obtained **PI-*b*-PEO(8)** was reacted with bromoacetyl bromide in pyridine at 0 °C. Compared with the ¹H NMR spectrum of **PI-*b*-PEO(8)**, the new resonance signal for methylene group protons (BrCH₂, -COOCH₂-) were detected at 4.05–4.40 ppm for **PI-*b*-PEO(9)** (Fig. 8), which proved successful esterification. Then the bromide atom on **PI-*b*-PEO(9)** was transformed into the azide group by azidation with the NaN₃ in DMF and the copolymer **PI-*b*-**

PEO(10) with an azide group at the conjunction point was achieved.

Although we could not clearly discriminate the protons connected to the azide group from ¹H NMR spectrum (Fig. 9), the -N₃ (2100 cm⁻¹) was observed from the FT-IR [Fig. 10(A)].

Synthesis and Characterization of 4-Miktoarm ABCD star(PS-*Pt*BA-PI-PEO) Quarterpolymer

Using the “click” chemistry between the propargyl group (on **PS-*b*-*Pt*BA(6)**) and the azide group (on **PI-*b*-PEO(10)**), the 4-Miktoarm ABCD star(PS-*Pt*BA-PEO-PI)(11) quarterpolymer was achieved (Scheme 2).

Typically, the reaction was proceeded in DMF using CuBr/PMDETA as catalyst system at 80 °C for 48 h. After the complete removal of copper salts by basic alumina column, the crude product was purified by ultra filtration mem-

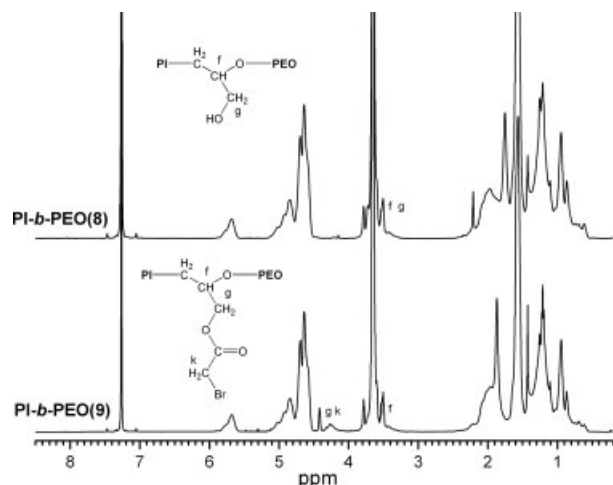


Figure 8. ¹H NMR spectrum (CDCl₃) of diblock copolymer **PI-*b*-PEO(8)** and **PI-*b*-PEO(9)**.

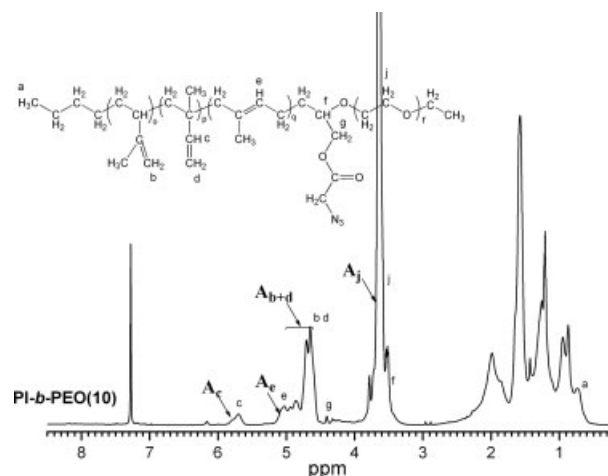


Figure 9. ¹H NMR spectrum (CDCl₃) of diblock copolymer **PI-*b*-PEO(10)**.

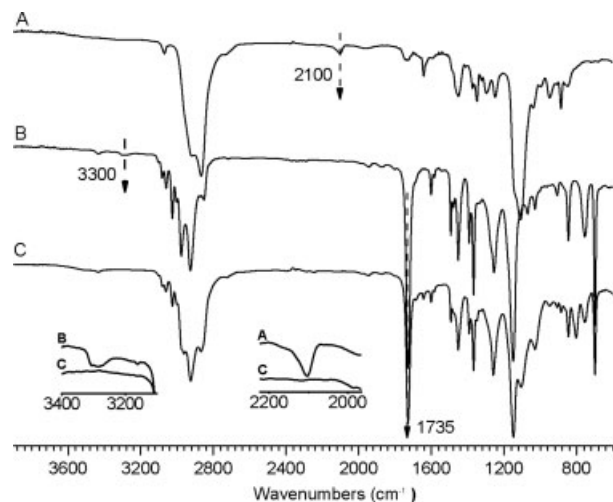


Figure 10. FT-IR spectra of (A) **PI-*b*-PEO(10)** with azide group (2100 cm^{-1}), (B) **PS-*b*-PtBA(6)** with propargyl group (3300 cm^{-1}) at the junction point and (C) **star(PS-PtBA-PEO-PI)(11)** quarterpolymer.

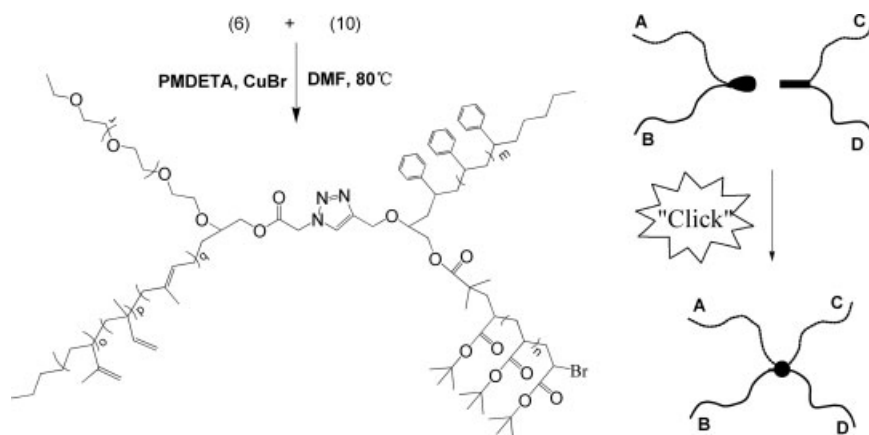
brane with methanol as the solvent, which was an efficient method to remove the small molecules and avoid the sample loss resulted from the common precipitation.

In this work, when we designed the 1:1 molar ratio of propargyl group (**PS-*b*-PtBA(6)**, $M_{n(\text{NMR})} = 6700$) to azide group (**PI-*b*-PEO(10)**, $M_{n(\text{NMR})} = 5800$), the final product would be a mixture of **PS-*b*-PtBA(6)**, **PI-*b*-PEO(10)**, and ABCD **star(PS-PtBA-PEO-PI)(11)** quarterpolymers and a complicated purification procedure must be followed. When the azide group was increased to 1.3 equiv., there was almost not any **PS-*b*-PtBA(6)** diblock copolymer could be

observed in final product. To guarantee the complete consumption of one component and simplify the separation procedure, the excessive **PI-*b*-PEO(10)** (1.3–1.7 equiv excess of $-\text{N}_3$ to propargyl group on **PS-*b*-PtBA(6)**) was deliberately used. Finally, the **PI-*b*-PEO(10)** could be removed from the target copolymer easily by mixed solvents of methanol/water.

Using the thin layer chromatography (TLC) method, it was found that the **PS-*b*-PtBA(6)** diblock copolymer had a R_f of almost 1.00 when THF was used as eluent, while the **PI-*b*-PEO(10)** and **star(PS-PtBA-PEO-PI)(11)** had a R_f of 0.10–0.20. Thus, we could trace the “click” reaction and discriminated the purification procedure according to the appearance and disappearance of the spot at R_f of 1.00.

In Figure 11, it was observed that a SEC curve (curve e, dot line) with a shoulder peak for the crude products appeared. By means of the TLC, the R_f of the crude product was in the range of the 0.10–0.20 and no spot at 1.00 could be detected, which meant there was almost not any **PS-*b*-PtBA(6)** diblock copolymer existed in the crude products and the shoulder peak in Figure 11(e) was attributed to the **PI-*b*-PEO(10)** diblock copolymer. Because the mixture of methanol/water was a good solvent for PEO segment but not for PS, PI, and PtBA segments, the **PI-*b*-PEO(10)** was first washed out selectively and then the monomodal curve (curve e, solid line) without a shoulder peak or tail was observed. The purification of quarterpolymers using this procedure was proved to be successful (Fig. 11). Compared with the SEC curves for diblock copolymer (b, **PS-*b*-PtBA**; d, **PI-*b*-PEO**), the



Scheme 2. Synthesis of 4-Miktoarm ABCD **star(PS-PtBA-PI-PEO)** quarterpolymers using the “click” chemistry.

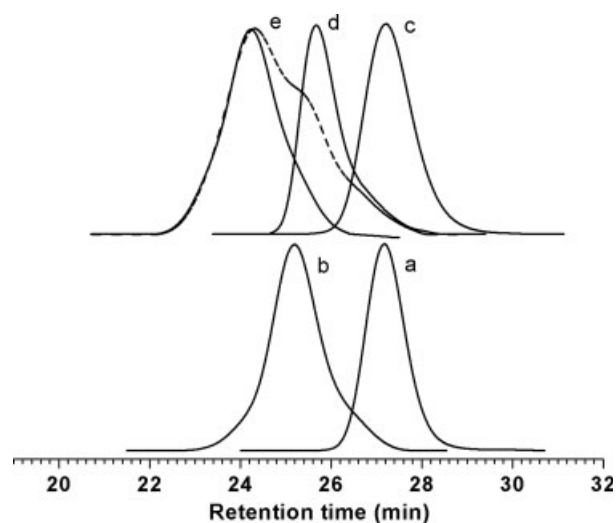


Figure 11. SEC curves of 4-Miktoarm star(PS-PtBA-PI-PEO) quarterpolymer (Exp. **11(A)**): a, **PS(5)**; b, **PS-*b*-PtBA(6)**; c, **PI(2)**; d, **PI-*b*-PEO(7)**; e, **star(PS-PtBA-PI-PEO)(11)**. (dot line: the copolymers before purification; solid line: the copolymer after purification).

curves for the crude and final quarterpolymer had an obvious shift to the shorter elution time.

Because of the smaller hydrodynamic volumes for the star-branched structures than the corresponding PS standard,¹⁰ the $M_{n(\text{SEC})}$ values of the quarterpolymers estimated by SEC were somewhat smaller than the predicted values and the actual M_n was determined by ^1H NMR. From the ^1H NMR spectrum of ABCD star(PS-

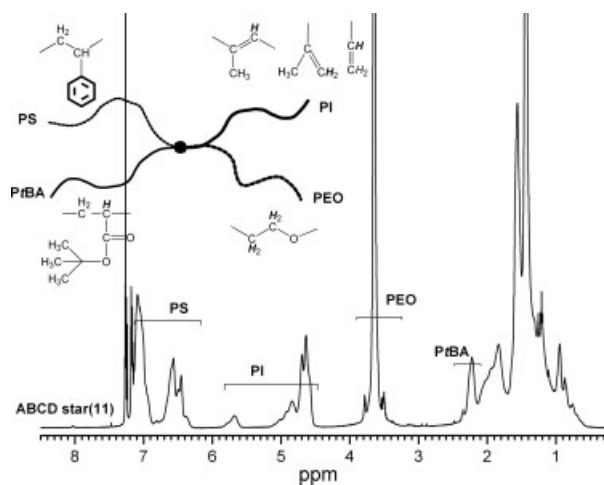


Figure 12. ^1H NMR spectrum (CDCl_3) of 4-Miktoarm ABCD star(PS-PtBA-PI-PEO) quarterpolymer.

PtBA-PEO-PI)(**11**) (Fig. 12), although the methylene protons ($-\text{CH}_2$ -triazole) connected to the formed triazole was overlapped by the protons ($(\text{CH}_3)\text{C}=\text{CH}_2$ of 3,4-addition, $-\text{CH}=\text{CH}_2$ of 1,2-addition) on PI arm at 4.63–4.95 ppm and could not be discriminated, the characteristic resonance signal for each block on the final star(PS-PtBA-PEO-PI)(**11**) quarterpolymer was observed clearly. Typically, the protons ($-\text{C}_6\text{H}_5$) at 6.30–7.30 ppm were attributed to the PS arm, the ones at 2.08–2.42 ppm were for PtBA arm, the ones at 5.70 ppm, 5.08 ppm, and 4.65–4.76 ppm were for PI arm, the ones at 3.53–3.70 ppm were for PEO arm. According to ^1H NMR spectra, the ratio of the monomer units

Table 3. Polymerization Data of star(PS-PtBA-PI-PEO)(**11**) Quarterpolymers and Their Intermediates^a

Exp.	star(PS-PtBA-PI-PEO)(11)				$N_S:N_{PtBA}:N_I:N_{EO}$ ^b		
	PS- <i>b</i> -PtBA(6)	PI- <i>b</i> -PEO(7)	$M_{n(\text{SEC})}$ (g/mol)	PDI	$M_{n(\text{NMR})}$ (g/mol)	Theoretical	Observed
(11A)	6700	5800			9300	1.20	11,900
(11B)	8900	5800	12,700	1.19	14,200	30:45:32:82	30:43:29:84
(11C)	8900	12000	18,800	1.20	21,200	30:45:66:170	30:48:60:178
(11D)	9100	12,000	17,700	1.21	22,100	63:20:66:170	63:26:60:185
(11E)	9100	7200	12,700	1.20	16,600	63:20:46:93	63:18:50:99
(11F)	15,400	7200	18,100	1.23	21,800	47:82:46:93	47:75:50:90
(11G)	15,400	12,000	23,200	1.26	27,900	47:82:66:170	47:79:71:183

^a $M_{n(\text{SEC})}$ and PDIs were determined by SEC with THF as solvent using PS standards. $M_{n(\text{NMR})}$ were calculated according to the ^1H NMR using the known $M_{n(\text{SEC})}$ of their precursors **PS(1)** and **PI(2)**, respectively.

^b $N_S:N_{PtBA}:N_I:N_{EO}$ represent the ratio of monomer units on star quarterpolymers, the theoretical value was calculated by weight composition theoretically and observed value was calculated according to ^1H NMR (see Fig. 12).

$N_S:N_{tBA}:N_I:N_{EO}$ on quarterpolymer was calculated, and the value was almost consistent with the expected structure (Table 3 and Fig. 12), which further confirmed the successful “click” procedure and ABCD star(PS-*Pt*BA-PI-PEO) quarterpolymer was successfully prepared.

From the FT-IR spectrum, we could also observe the existence of propargyl group ($-C\equiv CH$, 3304 cm^{-1}) [Fig. 10(B)] and the azide group ($-N_3$, 2100 cm^{-1}) [Fig. 10(A)] before the “click” chemistry, as well as the strong absorbance for ester group ($-COO-$, 1735 cm^{-1}), which further proved the successful synthesis of the diblock copolymer **PS-*b*-*Pt*BA(6)** and **PI-*b*-PEO(10)**, respectively. However, after the “click” chemistry between the two diblock copolymers [Fig. 10(C)], the disappearance of the characteristic absorbance for propargyl group (3300 cm^{-1}) and azide group (2100 cm^{-1}) in FT-IR spectrum verified the successful synthesis of star(PS-*Pt*BA-PI-PEO) quarterpolymer.

CONCLUSIONS

Well-defined ABCD star(PS-*Pt*BA-PEO-PI) quarterpolymers were prepared successfully by the “click” chemistry and multiple polymerization mechanism, in which the diblock copolymer with the propargyl group and azide group at the junction point were designed and synthesized, respectively, and used as the precursors. The structure of target quarterpolymers and all intermediates were well characterized by ^1H NMR, SEC, and FT-IR in detail. This work provided a versatile and efficient route to synthesize the star-shaped copolymers, on which the length of each arm could be tuned elaborately.

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