Synthesis of 4μ-PS₂PtBA₂, 4μ-PI₂PtBA₂, and 4μ-PI₂PS₂ Star-Shaped Copolymers by Combination of Glaser Coupling with Living Anionic Polymerization and ATRP

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Introduction. The star-shaped copolymers designed by connecting several chains into one point were endowed with some promising properties and applications.[1] However, the designing and synthesizing of star-shaped copolymers with scheduled compositions and arms were still a challenge for the researchers. For example, the synthesis of 4μ-A_2B_2 star-shaped showed greater difficulty because of its more complicated structure and statistical compositions.

Typically, using the coupling reaction between "living" polymeric species and chlorosilane, the 4μ-[poly(styrene)-(PS)]₂[poly(ethylene oxide)(PEO)]₂,[2] 4μ-PS₂[poly(isoprene)(PI)]₂, 4μ-PS₂[poly(butadiene) (PBd)]₂,[3] and 4μ-(PI)₂PBd₂[1b,c,4] were synthesized. Using the nonpolymerizable "double diphenylethylene" (DDPE) or its derivatives, the 4μ-PS₂PBd₂, 4μ-PS₂PI₂, 4μ-PS₂(PBd-b-PS)₂,[5] 4μ-PI₂[poly(methyl methacrylate)(PMMA)]₂,[6] 4μ-PS₂PI₂,[4b] 4μ-[poly(isobutylene)(PIB)]₂-[poly(methyl vinyl ether)(PMeVE)]₂,[7] and 4μ-PS₂PI₂[8] were also obtained. Obviously, the above two strategies were always involved the high-vacuum techniques, troublesome procedures, and limitations to the monomers adapted to living anionic polymerization (LAP) mechanism. Thus, the mechanism transformation[9] had been developed for 4μ-(PS)₂/[poly(1,3-dioxepane)(PDOP)]₂,[10] 4μ-(PS)₂/[poly(tetrahydrofuran)(PTHF)]₂,[11] 4μ-PS₂PEO₂,[12] 4μ-(PS)₂/[poly(ε-caprolactone)(PCL)]₂ and 4μ-(PS)₂/[poly(*tert*-butyl methacrylate)(PtBuMA)]₂,[13] 4μ-(PCL)₂ [poly[6-(4-methoxy-4-oxyazobenzene)hexyl methacrylate] (PMMAZO)]₂,[14] 4μ-[poly(*tert*-butyl acrylate)(PtBA)]₂[poly(vinyl acetate)(PVAc)]₂, and 4μ-[poly(acrylic acid)(PAA)]₂ (PVAc)₂.[15] However, using this method, it should be careful to deal with the designing and synthesizing of a hetero-tetrafunctional initiator, and the functional groups transformation for different polymerization mechanisms might be repellent. Recently, Tunca et al. used a homo-coupling reaction of alkyne at the junction point of diblock copolymers for 4μ-(PS)₂(PMMA)₂ and 4μ-(PCL)₂(PS)₂.[16] However, a complicated catalytic system of (PPh₃)₂PdCl₂/PPh₃/CuI, a trifunctional initiator, a solvent mixture of triethylamine (Et₃N)/acetonitrile (CH₃CN), and a longer time of 72 h should be involved.

On the other hand, the LAP mechanism was rarely combined with other "living"/controlled polymerization mechanisms for construction of 4μ-A_2B_2 star-shaped copolymers, such as 4μ-PI₂PtBA₂, 4μ-PI₂PtBA₂, and amphiphilic 4μ-PS₂-PAA₂, 4μ-PI₂PAA₂. And interestingly, the PI was a classical soft segment in the investigation of multiblock and multiconstitution copolymers, which might bring the copolymers

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with special properties.[17] Thus, looking for a novel and versatile protocol for these 4μ-A_2B_2 star-shaped copolymers was still a significant work. Herein, the alkyne−alkyne Glaser coupling was provided in the presence of a simple system of pyridine/CuBr/*N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA)[18] to prepare the precursors with two initiating sites at junction point, and 4μ-A_2B_2 star-shaped copolymers were then obtained by the atom transfer radical polymerization (ATRP) mechanism.

Results and Discussion. According to our previous work,[19] **PS(1)** ($M_{n(SEC)}$ = 4900 g/mol) or **PI(1)** ($M_{n(SEC)}$ = 4600 g/mol) with an active and a protected hydroxyl group at the ω-end were synthesized by capping poly(styryl)lithium (PS⁻Li⁺) or poly(isoprene)lithium (PIS⁻Li⁺) with ethoxyethyl glycidyl ether (EEGE), and then **PS(2)** or **PI(2)** was obtained by selective modification of active hydroxyl groups with propargyl bromide in the diphenylmethylpotassium (DPMK)/tetrahydrofuran (THF) system at 0 °C (Scheme 1). The ¹H NMR spectra of **PS(1)**, **PS(2)**, **PI(1)**, and **PI(2)** are provided in Figures S1−S4 (see Supporting Information), respectively. According to ¹H NMR spectra, the transformation efficiency of hydroxyl groups into alkyne groups (99.52% for $EF_{PS(2)}$ and 99.70% for $EF_{PI(2)}$) were obtained with high values (Table S1, see Supporting Information).

In the presence of the pyridine/PMDETA/CuBr system, the Glaser coupling between alkyne and alkyne groups (at **PS(2)** or **PI(2)** end) proceeded at room temperature for 24 h, and **PS(3)** ($M_{n(SEC)}$ = 10 000 g/mol) or **PI(3)** ($M_{n(SEC)}$ = 9200 g/mol) with two protected hydroxyl groups at junction point was obtained. From the SEC curves of their hydrolyzed product **PS(4)** or **PI(4)** (which would be discussed in the following section, Figure 1A,B), the monomodal peaks with low PDIs as that for **PS(3)** or **PI(3)** were observed. Comparing with their precursors **PS(1)** or **PI(1)**, it was found that the SEC curves of coupled product shift to lower elution time, and there were almost not any tail peaks corresponding to their precursors at the longer elution time, which showed that the Glaser coupling was rather efficient and finished with efficiency of almost 100% ($EF_{PS(3)}$ or $EF_{PI(3)}$). From FT-IR spectra (Figures S5 and S6, see Supporting Information), we could observed that the stretch absorption at 3304 cm⁻¹ for the alkyne group (−C≡CH) on **PS(2)** or **PI(2)** end completely disappeared in spectra for **PS(3)** or **PI(3)**, which further confirmed the success of Glaser coupling reaction.

The precursor **PS(4)** or **PI(4)** with two active hydroxyl groups at junction point was obtained by the hydrolysis of protected groups in the THF/HCl aqueous solution (37%) system. According to our previous work,[19] this process was also rather complete (100% for $EF_{PS(4)}$ and $EF_{PI(4)}$) by analyzing the disappearance of the resonance signal of the methyne group proton (−OC*H*(CH₃)O−) from ¹H NMR spectra at 4.70 ppm (Figure 2A,C). Subsequently, using pyridine as medium, the recovered hydroxyl groups at junction point of **PS(4)** or **PI(4)** were esterified with 2-bromoisobutyryl bromide at 0 °C for 24.0 h for macroinitiators **PS(5)** and **PI(5)** with two 2-bromoisobutyryl groups at the junction point. Because of the overlapping of the resonance signal of methylene group protons (−C*H₂*COO−) and that of methylene group protons (−OC*H₂*C≡C−) at 3.84−4.18 ppm, it was observed that the intensity of resonance signals at 3.84−4.18 ppm increased and that of resonance signals at

Scheme 1. Synthesis Procedure for 4μ-A$_2$B$_2$ Star-Shaped Copolymers
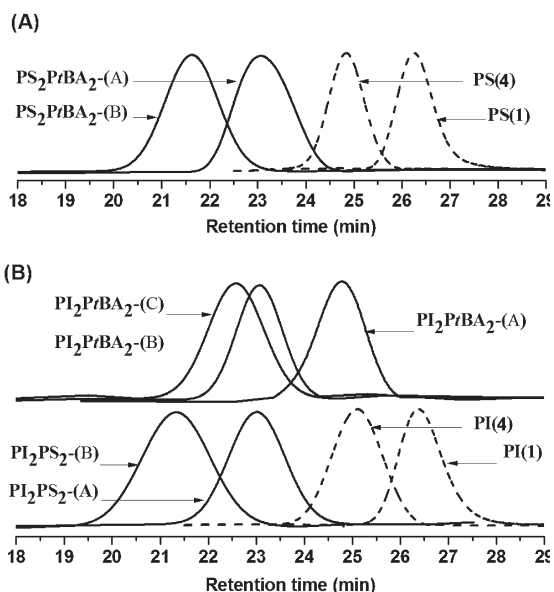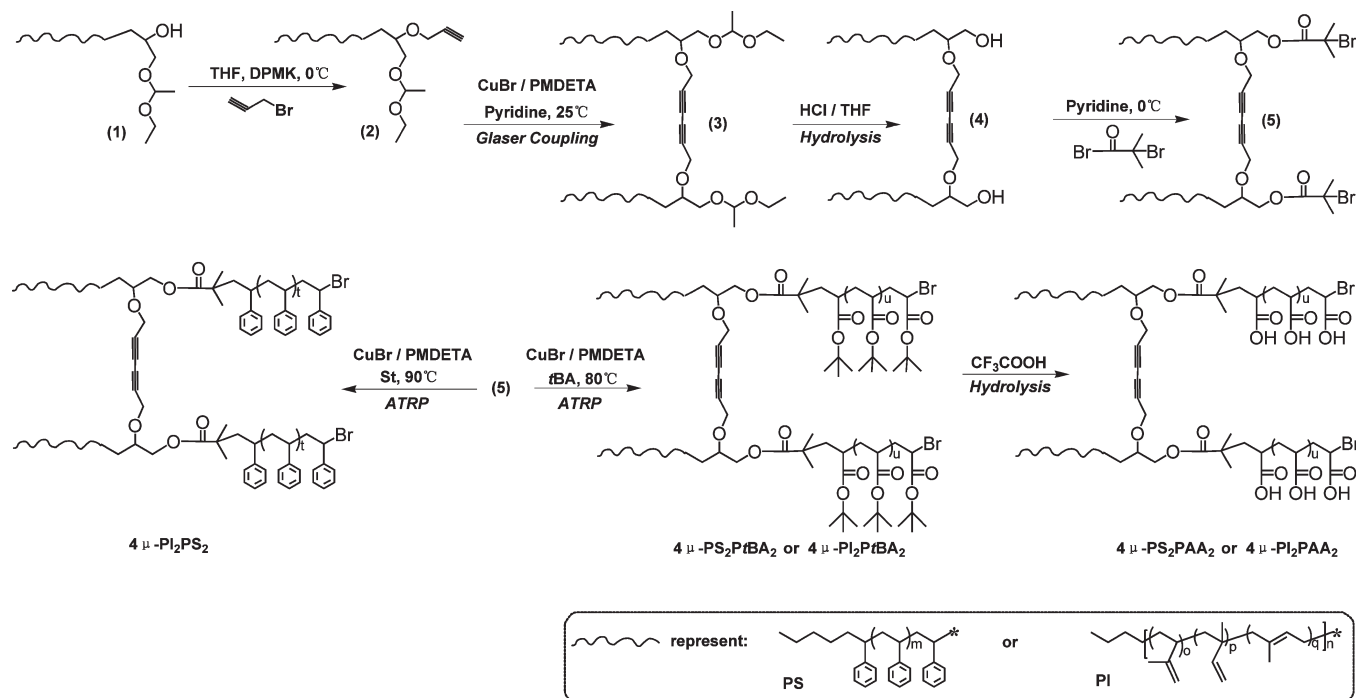
Figure 1. SEC curves of 4μ-A$_2$B$_2$ star-shaped copolymers, **PS(4)**, **PI(4)**, and their precursors **PS(1)** and **PI(1)**.

3.34−3.65 ppm decreased simultaneously from ^{1}H NMR (Figure 2B,D). The cause might be that once the esterification procedure was finished and the ester bond was formed, the resonance signal of protons (−CH_2OH) at 3.34−3.65 ppm (in Figure 2A,C) was transformed into the resonance signal of protons (−CH_2COO−) at 3.84−4.18 ppm (in Figure 2B,D) immediately. Additionally, the characteristic signals of methyl protons (−C(CH_3)$_2$Br) were also observed at 1.94 ppm. According to ^{1}H NMR spectra, the esterification efficiencies (99.91% for EF$_{PS(5)}$ and 99.54% for EF$_{PI(5)}$) of hydroxyl groups were calculated by using formulas S7 and S8, respectively (Table S2, see Supporting Information).

Using FT-IR measurement (Figure S7, see Supporting Information), it was found that the stretch absorption for

ester carbonyl (−COO−) on **PS(5)** or **PI(5)** was all discriminated at 1740 cm^{-1}, which further proved the successful transformation of hydroxyl groups into 2-bromoisobutyryl groups.

The transformation procedure from **PS(1)** to **PS(4)** (or **PI(1)** to **PI(4)**) was also traced by MALDI-TOF mass spectra. From example (Figure 3), it was observed an increase of 38.0 Da from peak (C$_4$H$_9$−(C$_8$H$_8$)$_{41}$−C$_7$H$_{15}$O$_3$·Ag$^+$ = 4585.6 Da) of **PS(1)** to peak (C$_4$H$_9$−(C$_8$H$_8$)$_{41}$−C$_7$H$_{14}$O$_3$−C$_3$H$_3$·Ag$^+$ = 4622.6 Da) of **PS(2)**, which corresponds to the successful modification of an alkyne group onto the PS end. After Glaser coupling, the peak for **PS(3)** chain was again shifted to (C$_4$H$_9$)$_2$−((C$_8$H$_8$)$_{41}$)$_2$−(C$_7$H$_{14}$O$_3$)$_2$−(C$_3$H$_2$)$_2$·Ag$^+$ = (4622.6 − 108.0) × 2 − 2.0 + 108.0 = 9135.2 Da. Once two ethoxyethyl groups ((C$_4$H$_9$O)$_2$ = 146.1 Da) at the junction point were removed by hydrolysis, the peak for **PS(4)** again shifted to (C$_4$H$_9$)$_2$−((C$_8$H$_8$)$_{41}$)$_2$−(C$_3$H$_6$O$_2$)$_2$−(C$_3$H$_2$)$_2$·Ag$^+$ = 9135.2 − 146.1 + 2.0 = 8991.1 Da. These results also affirmed the successful synthesis of **PS(4)**.

Using **PS(5)** or **PI(5)** as macroinitiators, PMDETA/CuBr as catalyst system, and toluene as solvent, the ATRP of St proceeded under 90 °C for 4μ-PI$_2$PS$_2$ star-shaped copolymers, and that of tBA proceeded under 80 °C for 4μ-PS$_2$PtBA_2 and 4μ-PI$_2$PtBA_2 star-shaped copolymers (Scheme 1). From Figure 1, we could discriminate that all SEC curves of star-shaped copolymers had clear shift to the shorter elution time, which proved the successful ATRP of all monomers under certain conditions.

From ^{1}H NMR spectra (Figure S8, see Supporting Information), the characteristic resonance signals at 6.30−7.30 ppm for aromatic protons (−C$_6$H$_5$) on PS arms and the characteristic resonance signals at 2.08−2.44 ppm for methyne group protons (−CH$_2$CH−), at 0.80−1.90 ppm for methyl group protons (−C(CH_3)$_2$− and (CH_3)$_3$C−), and at 4.30−4.55 ppm for protons (−CH(COO−)Br and −CH_2COO−) on PtBA arms were clearly discriminated in their separate spectrum. Similarly, from ^{1}H NMR spectra (Figure S8, see Supporting Information), the characteristic resonance signals at 5.70 ppm attributed to methyne protons (−CH=CH$_2$) and at 4.85 ppm attributed to methylene

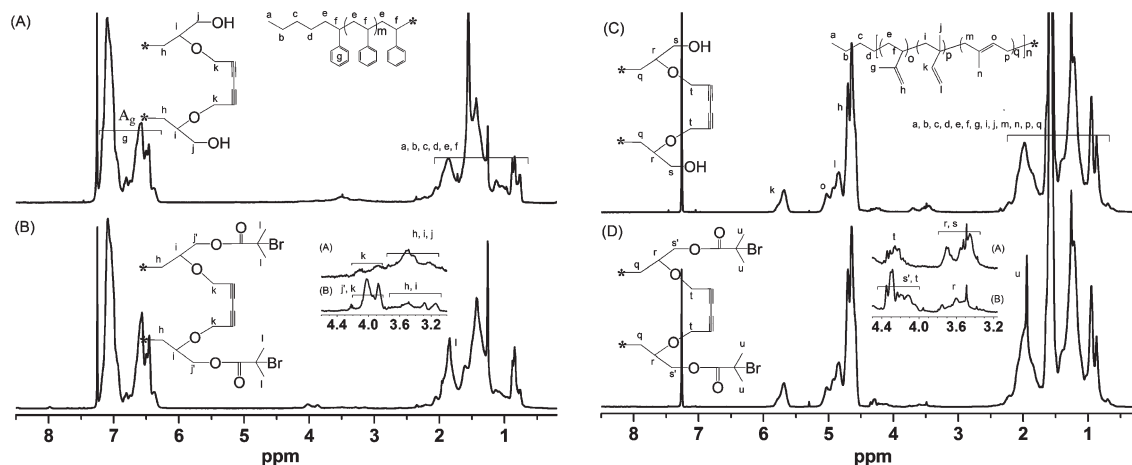**Figure 2.** ^{1}H NMR spectra of **PS(4)** (A), **PS(5)** (B), **PI(4)** (C), and **PI(5)** (D) (in CDCl$_3$).
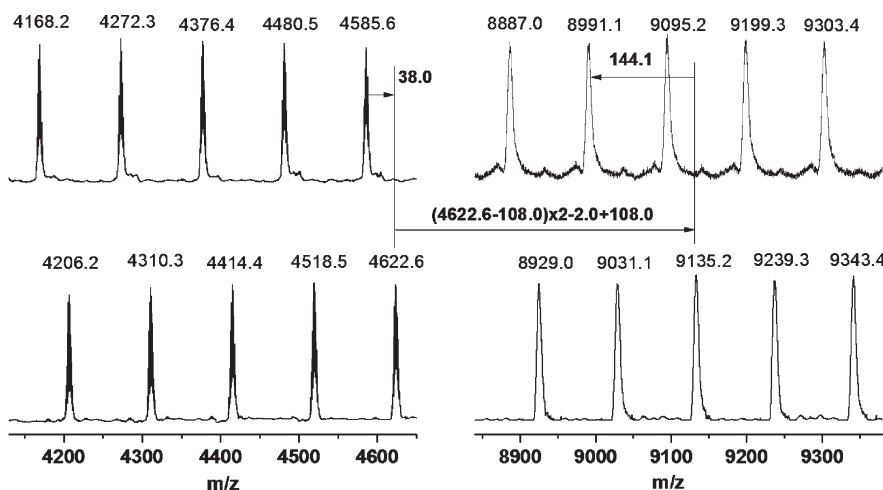

Figure 3. MALDI-TOF mass spectra of **PS(1), PS(2), PS(3),** and **PS(4)**.

Table 1. Data of 4μ-A$_2$B$_2$ Star-Shaped Copolymers

	star-shaped copolymers					
entry[a]	$M_{n(SEC)}$[b] (g/mol)	PDI[b]	$M_{n(NMR)}$[c] (g/mol)	N_{St}[d]	N_{Is}[d]	$N_{tBA/AA}$[d]
4μ-PS$_2$PtBA$_2$ (A)	23 700	1.13	24 600	48		55
4μ-PS$_2$PtBA$_2$ (B)	61 600	1.15	54 100	48		171
4μ-PS$_2$PAA$_2$ (A)			18 400	48		55
4μ-PS$_2$PAA$_2$ (B)			34 900	48		171
4μ-PI$_2$PS$_2$ (A)	25 400	1.17	24 500	69	71	
4μ-PI$_2$PS$_2$ (B)	54 700	1.20	49 300	188	71	
4μ-PI$_2$PtBA$_2$ (A)	10 900	1.14	12 600		71	10
4μ-PI$_2$PtBA$_2$ (B)	24 300	1.15	21 200		71	43
4μ-PI$_2$PtBA$_2$ (C)	31 700	1.17	29 100		71	74
4μ-PI$_2$PAA$_2$ (A)			11 500		71	10
4μ-PI$_2$PAA$_2$ (B)			16 300		71	43
4μ-PI$_2$PAA$_2$ (C)			20 800		71	74

[a] The A, B, and C in parentheses represent the different series. [b] Determined by SEC with THF as solvent using PS standards. [c] The molecular weights of star-shaped copolymers were calculated according to ^{1}H NMR (Figure S8, see Supporting Information). [d] The N_{St}, N_{Is}, and $N_{tBA/AA}$ represent the numbers of styrene, isoprene, and *tert*-butyl acrylate or acrylic acid units on each arm.

protons ($-CH=CH_2$) of 1,2-addition, at 4.49−4.77 ppm attributed to methylene protons of 3,4-addition ($-C(CH_3)=CH_2$) and at 5.05 ppm attributed to methyne protons ($-CH=C(CH_3)-$) of 1,4-addition were also observed. According to ^{1}H NMR spectra, the molecular weights of obtained star-shaped copolymers were derived (Table 1). Finally, the *tert*-butyl groups on PtBA segment could be easily and selectively removed under the trifluoroacetic acid (TFA)/dichloromethane (CH$_2$Cl$_2$) system for 24.0 h,[20] and the amp-

hiphilic copolymers 4μ-PS$_2$PAA$_2$ and 4μ-PI$_2$PAA$_2$ star-shaped copolymers were also achieved.

The 4μ-A$_2$B$_2$ star-shaped copolymers were further verified by FT-IR (Figures S9 and S10, see Supporting Information). In spectra of 4μ-PS$_2$PtBA$_2$ or 4μ-PI$_2$PtBA$_2$, the absorptions for characteristic ester carbonyl ($-COO-$) on PtBA arms were all discriminated clearly at 1733 cm^{-1}. After the PtBA arms were transformed into PAA arms, the absorptions for acid carbonyl ($-COOH$) at 1741 cm^{-1} and the broad band

for hydroxyl (−OH) at 2390−3700 cm^{-1} attributed to 4μ-PS$_2$PAA$_2$ or 4μ-PI$_2$PAA$_2$ were also observed. These FT-IR results were well consistent with the copolymer structure characterized above.

In conclusion, the 4μ-A$_2$B$_2$ star-shaped copolymers containing PS, PI, PtBA, or PAA arms were synthesized by Glaser coupling and multiple polymerization mechanisms (LAP and ATRP), and the target copolymers were well characterized by SEC, MALDI-TOF mass spectra, FT-IR, and ^{1}H NMR in detail. In this paper, the condition of Glaser coupling was largely simplified, and LAP was successfully combined with ATRP mechanism. Our work provided a versatile strategy to 4μ-A$_2$B$_2$ star-shaped copolymers with various compositions.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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