Synthesis of 4μ-PS2PrBA2, 4μ-PI2PrBA2, 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-A2B2 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, 4μ-PS2poly(isoprene) (PI)2, 4μ-PS2poly(butadiene) (PB)2, and 4μ-PI2PBd2 was synthesized. Using the nonpolymerizable “double di-phenylethylene” (DDPE) or its derivatives, the 4μ-PS2PBd2, 4μ-PI2PBd2, 4μ-PS2PB(Ph-b-PS)2, 4μ-PS2poly(methyl methacrylate)(PMMA)2, 4μ-PS2PI2, 4μ-PI2poly(isobutylenylene)(PBI)2, [poly(methyl vinyl ether)](PMVe)2, and 4μ-PS2PI2 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 had been developed for 4μ-(PS)2/poly(1,3-dioxepane)(PDOP)2, 4μ-(PS)2/poly(tetrahydrofuran)(THF)2, 4μ-PS2PEO2, 4μ-PS2poly(e-caprolactone)(PCL)2, and 4μ-PS2/poly(tert-butyll methacrylate) (PrBuMA)2. The 4μ-(PCL)2/poly([6-(4-methoxy-4-oxazobenzene)hexyl methacrylate](PMMAZO))2, 4μ-[poly(tert-butyll acrylate)(PrBuA)]2/poly(vinyl acetate)(PVAc)2, and 4μ-[poly(acrylic acid)(PAA)]2/poly(Styrene)2 were also obtained. 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 homocoupling reaction of alkylene at the junction point of diblock copolymers for 4μ-(PS)2(PMMA)2, and 4μ-(PCL)2(PCL)2.16 However, a complicated catlytic system of (PPh3)2PdCl2/PPh3/CuI, a trifunctional initiator, a solvent mixture of tri-ethylamine (Et3N)/acetoniitrile (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-A2B2 star-shaped copolymers, such as 4μ-PI2PrBA2, 4μ-PI2PrBA2, and amphiliphic 4μ-PS2-PA2A2, 4μ-PI2-PA2A2. And interestingly, the PI was a classical soft segment in the investigation of multiblock and multiconstitution copolymers, which might bring the copolymers with special properties.17 Thus, looking for a novel and versatile protocol for these 4μ-A2B2 star-shaped copolymers was still a significant work. Herein, the alkyl–alkyl Glaser coupling was provided in the presence of a simple system of pyridine/CuBr/N,N,N’,N’’,N’’’-pentamethydiethylenetriamine (PMDETA)18 to prepare the precursors with two initiating sites at junction point, and 4μ-A2B2 star-shaped copolymers were then obtained by the atom transfer radical polymerization (ATRP) mechanism.

Results and Discussion. According to our previous work,19 PI(1) (Mn(SEC) = 4900 g/mol) or PI(1) (Mn(SEC) = 4600 g/mol) with an active and a protected hydroxyl group at the α-end were synthesized by capping poly(styryl)lithium (PS Li+) or poly(isoprenyl)lithium (PS 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 diphenylihromassium (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 alkylene groups (99.52% for EFPS(2) and 99.70% for EFPI(2)) were obtained with high values (Table S1, see Supporting Information).

In the presence of the pyridine/PMDETA/CuBr system, the Glaser coupling between alkylene and alkylene groups (at PS(2) or PI(2) end) proceeded at room temperature for 24 h, and PS(3) (Mn(SEC) = 10 000 g/mol) or PI(3) (Mn(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% (EFPS(3) or EFPI(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 alkylene group (−C=C=H) 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 precursors 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 EFPS(4) and EFPI(4)) by analyzing the disappearance of the resonance signal of the methylene group proton (−OCH(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 (−CH2COO−) and that of methylene group protons (−OCH2C≡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...
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 ($\text{-C}_2\text{H}_5\text{OH}$) at 3.34–3.65 ppm (in Figure 2A, C) was transformed into the resonance signal of protons ($\text{-C}_2\text{H}_5\text{COO}$) at 3.84–4.18 ppm (in Figure 2B, D) immediately. Additionally, the characteristic signals of methyl protons ($\text{-C}(_3\text{H}_7)\text{Br}$) were also observed at 1.94 ppm. According to $^1$H NMR spectra, the esterification efficiencies (99.91% for EF$_{\text{PS}(5)}$ and 99.54% for EF$_{\text{PI}(5)}$) 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 ($\text{-COO}^-$) 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$_8$)$_4$1-C$_7$H$_15$O$_3$3-Ag$^+$ = 4585.6 Da) of PS(1) to peak (C$_4$H$_9$-(_C$_8$H$_8$)$_4$1-C$_7$H$_14$O$_3$-C$_3$H$_3$3-Ag$^+$ = 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$_8$)$_2$1-(_C$_7$H$_14$O$_3$)$_2$-(_C$_3$H$_2$)$_2$3-Ag$^+$ = (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$_8$)$_2$1-(_C$_7$H$_14$O$_3$)$_2$-(_C$_3$H$_2$)$_2$3-Ag$^+$ = 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-PS$_2$PtBA$_2$ and 4μ-PI$_2$PtBA$_2$ star-shaped copolymers, and that of B 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 5.70 ppm attributed to methyne protons ($\text{-C}_2\text{H}_2\text{CH}_2$) and at 4.85 ppm attributed to methylene groups 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 ($\text{-C}_2\text{H}_2\text{CH}_2$) and at 4.85 ppm attributed to methylene groups 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 ($\text{-C}_2\text{H}_2\text{CH}_2$) and at 4.85 ppm attributed to methylene groups.
protons (−CH=CH₂) of 1,2-addition, at 4.49–4.77 ppm attributed to methylene protons of 3,4-addition (−C(CH₃)=CH₂) and at 5.05 ppm attributed to methyne protons (−CH=CH(C₃H₃)=) of 1,4-addition were also observed. According to ¹H NMR spectra, the molecular weights of obtained star-shaped copolymers were derived (Table 1). Finally, the tert-buty1 groups on P₄tBA segment could be easily and selectively removed under the trifluoroacetic acid (TFA)/dichloromethane (CH₂Cl₂) system for 24.0 h, and the amphiphilic copolymers 4µ-PS₂PAA₂ and 4µ-PI₂PAA₂ star-shaped copolymers were also achieved.

The 4µ-A₂B₂ star-shaped copolymers were further verified by FT-IR (Figures S9 and S10, see Supporting Information). In spectra of 4µ-PS₂PrBA₂ or 4µ-PI₂PrBA₂, the absorptions for characteristic ester carbonyl (−COO−) on PrBA arms were all discriminated clearly at 1733 cm⁻¹. After the PrBA arms were transformed into PAA arms, the absorptions for acid carbonyl (−COOH) at 1741 cm⁻¹ and the broad band

Table 1. Data of 4µ-A₂B₂ Star-Shaped Copolymers

<table>
<thead>
<tr>
<th>entry</th>
<th>M(SEC) (g/mol)</th>
<th>PDI</th>
<th>M(NMR) (g/mol)</th>
<th>N₃St</th>
<th>N₃Is</th>
<th>N₄tBA/AA</th>
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<tr>
<td>4µ-PS₂PBA₂ (A)</td>
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<td>1.13</td>
<td>24 600</td>
<td>48</td>
<td>55</td>
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<tr>
<td>4µ-PS₂PBA₂ (B)</td>
<td>61 600</td>
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<td>54 100</td>
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<tr>
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<td>1.20</td>
<td>18 400</td>
<td>48</td>
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</tr>
<tr>
<td>4µ-PS₂PAA₂ (B)</td>
<td>34 900</td>
<td>1.14</td>
<td>34 900</td>
<td>48</td>
<td>171</td>
<td></td>
</tr>
<tr>
<td>4µ-PI₂PS₂ (A)</td>
<td>25 400</td>
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<td>24 500</td>
<td>69</td>
<td>71</td>
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<tr>
<td>4µ-PI₂PS₂ (B)</td>
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<td>49 300</td>
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<td>71</td>
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<tr>
<td>4µ-PI₂PBA₂ (A)</td>
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<td>1.14</td>
<td>12 600</td>
<td>71</td>
<td>10</td>
<td></td>
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<tr>
<td>4µ-PI₂PBA₂ (B)</td>
<td>24 300</td>
<td>1.15</td>
<td>21 200</td>
<td>71</td>
<td>43</td>
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<tr>
<td>4µ-PI₂PBA₂ (C)</td>
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<td>1.17</td>
<td>29 100</td>
<td>71</td>
<td>74</td>
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<tr>
<td>4µ-PI₂PAA₂ (A)</td>
<td>11 500</td>
<td>1.20</td>
<td>11 500</td>
<td>71</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>4µ-PI₂PAA₂ (B)</td>
<td>16 300</td>
<td>1.15</td>
<td>16 300</td>
<td>71</td>
<td>43</td>
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<tr>
<td>4µ-PI₂PAA₂ (C)</td>
<td>20 800</td>
<td>1.17</td>
<td>20 800</td>
<td>71</td>
<td>74</td>
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</table>

* The A, B, and C in parentheses represent the different series. Determined by SEC with THF as solvent using PS standards. * The molecular weights of star-shaped copolymers were calculated according to ¹H NMR (Figure S8, see Supporting Information). * The N₃St, N₃Is, and N₄BA/AA represent the numbers of styrene, isoprene, and tert-butyl acrylate or acrylic acid units on each arm.
for hydroxyl (−OH) at 2390−3700 cm\(^{-1}\) attributed to 4μ-
PS\(_2\)PAA\(_2\) or 4μ-PI\(_3\)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 con-
taining PS, PI, PrBA, 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.

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

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