

*Supporting Information for*

The Effect of Chain Architecture on the Phase Behavior  
of A<sub>4</sub>B<sub>4</sub> Miktoarm Block Copolymers

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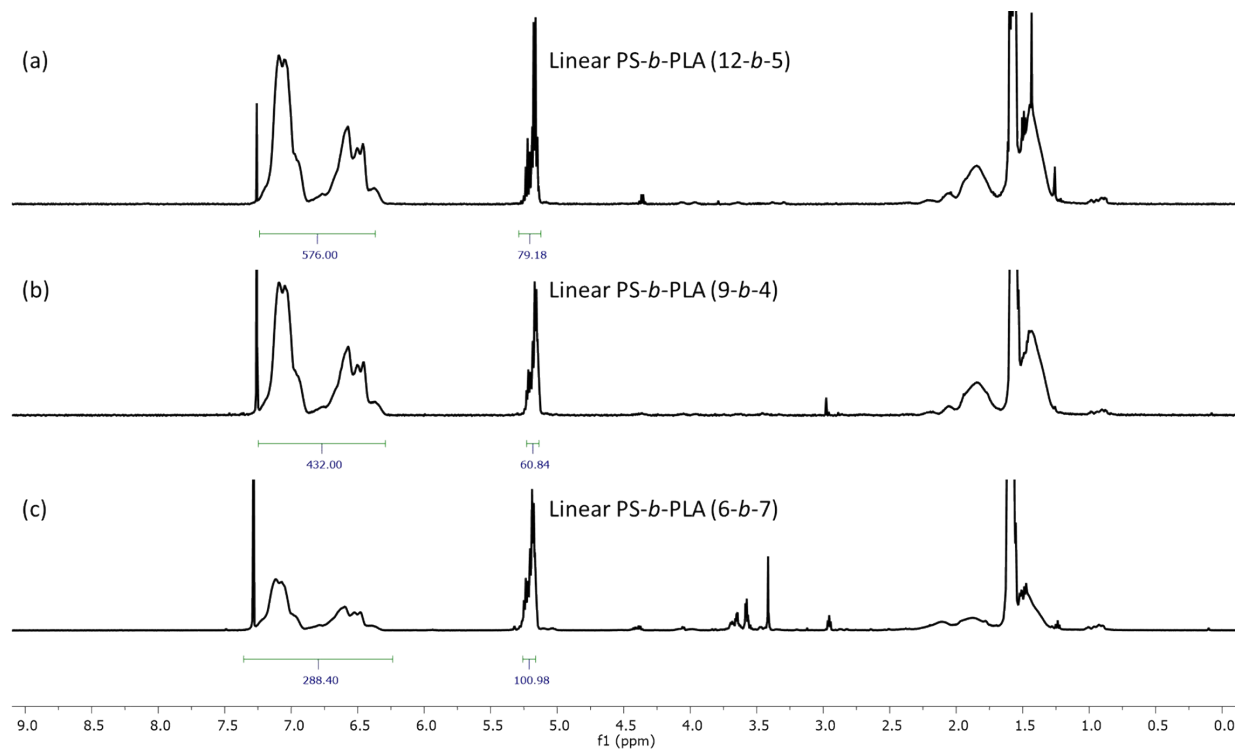
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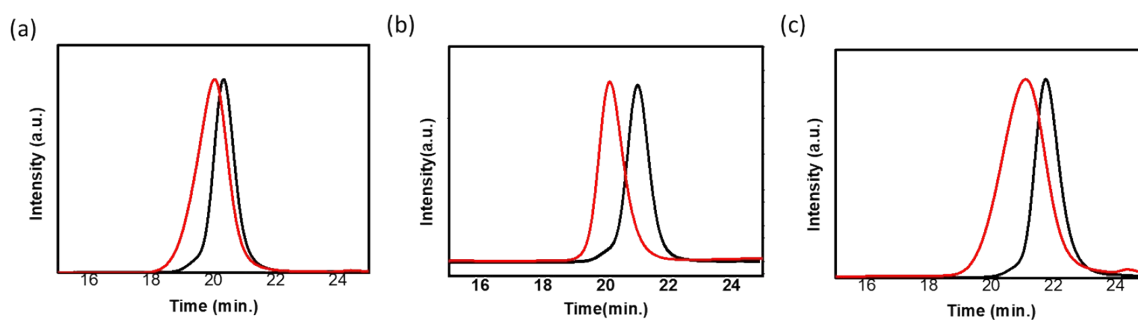
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## Experimental Methods

Figure S1 is  $^1\text{H-NMR}$  spectrum of linear PS-*b*-PLA BCPs. Integration in the 6.4~7.2 ppm is for the polystyrene (PS) and the integration in the 5.1~5.3 ppm is for the polylactic acid (PLA).



**Figure S1.**  $^1\text{H-NMR}$  spectrum of linear PS-*b*-PLA BCPs, (a) SL12-5, (b) SL9-4, and (c) SL6-7.



**Figure S2.** GPC traces of (a) SL12-5, (b) SL9-4, and (c) MSL6-7. Black lines represent hydroxyl terminated linear PS grown via atom transfer radical polymerization, and red lines represent PS-*b*-PLA BCPs after ROP.

## Synthesis of Linear Block Copolymers

### Synthesis of Linear PS-*b*-PLA BCP (SL9-4)

HEBib (0.1g, 0.4738mmol) was added dropwise into a 50mL vial along with Styrene (8.5g, 81.61mmol), Anisole (8.5g, 78.60mmol) and PMDETA(0.082g, 0.4738mmol). The mixture was well mixed before being put into a Schrenk flask. After three times of freeze pump thaw with argon backfilling, the Schrenk flask was put into an oil bath with preset temperature of 110°C. After some time has passed, CuBr(I) (0.06794g, 0.4738mmol) was added as catalyst for the ATRP to begin. The reaction was left to go on for 3 hours and the target molecular weight was monitored by GPC. The reaction mixture was cooled to room temperature and precipitated into cold methanol. The product was dissolved in THF and was passed through an aluminum oxide column in order to remove copper complex. Afterwards, the mixture was again precipitated into methanol. After drying for two full days, the hydroxyl terminated polystyrene (PS-OH9k,  $M_n = 9.0$  kg/mol) was collected into a 50mL vial. The molecular weight was confirmed by GPC as it can be seen in Figure S2(b). Ring opening polymerization (ROP) was used for polymerization of polylactic acid (PLA). PS-OH9k (1g, 0.111mmol) was weighed and added to a 50mL vial along with DCM (3mL) and D,L-Lactide (0.9259g, 6.423mmol). The mixture was well mixed and moved to a Schrenk flask. The flask was argon purged for 30 minutes and 1,8-Diazabicyclo(5.4.0)undec-7-ene (0.0169g, 0.111mmol) as catalyst for the reaction. The ROP reaction was left to go on for 3 hours and benzoic acid (0.0136g, 0.111mmol) was added to quench the reaction. The mixture was left to be stirred for another 10 minutes and precipitated in methanol. The resulting PS-*b*-PLA BCP

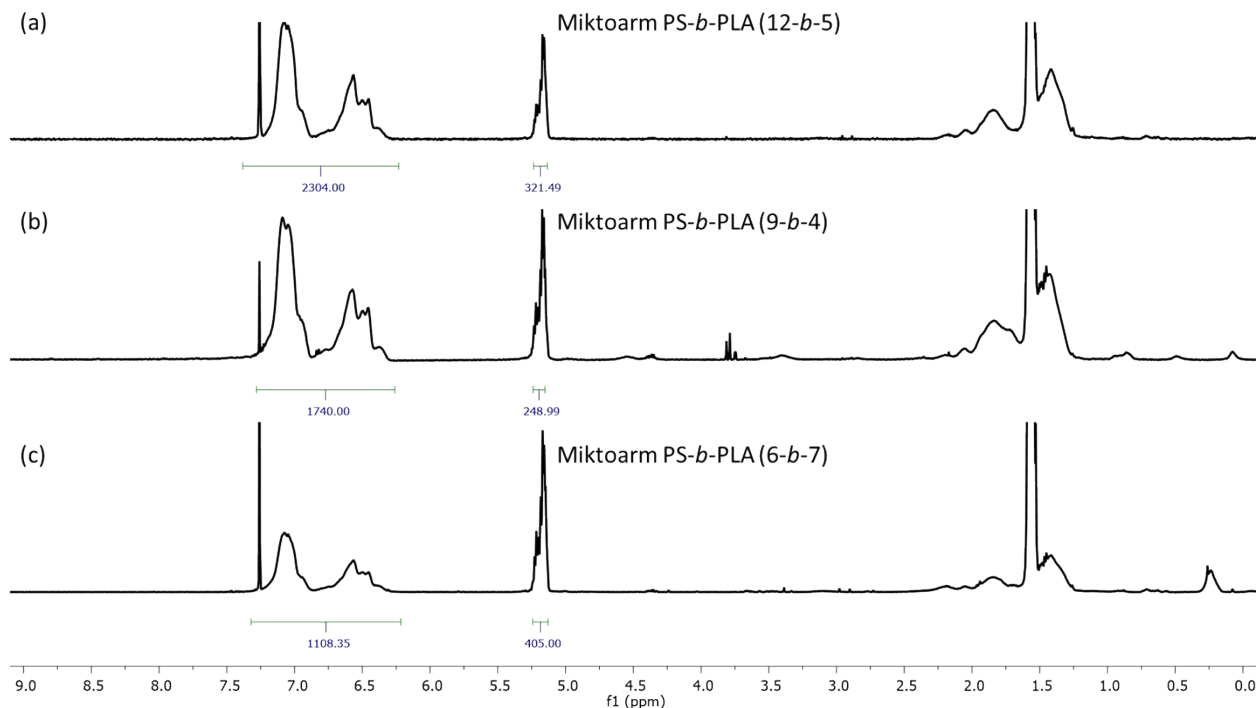
was dried in a vacuum oven for two full days. The molecular weight was confirmed by GPC (Figure S2(b)), and its PS to PLA ratio was confirmed by NMR in Figure S1(b).

### **Synthesis of Linear PS-*b*-PLA BCP (SL6-7)**

HEBib (0.1g, 0.4738mmol) was added dropwise into a 50mL vial along with Styrene (6g, 57.61mmol), Anisole (6g, 55.48mmol) and PMDETA (0.082g, 0.4738mmol). The mixture was well mixed before being put into a Schrenk flask. After three freeze pump thaw with argon backfilling, the Schrenk flask was put into an oil bath with preset temperature of 110°C. After some time has passed, CuBr(I) (0.06794g, 0.4738mmol) was added as catalyst for the ATRP to begin. The reaction was left to go on for 3 hours and the target molecular weight was monitored by GPC. The reaction mixture was cooled to room temperature and precipitated into cold methanol. The product was dissolved in THF and was passed through an aluminum oxide column in order to remove copper complex. After copper removal, the mixture was again precipitated into methanol. After thorough drying for two full days, the hydroxyl terminated polystyrene (PS-OH6k,  $M_n = 6.0$  kg/mol) was collected into a 50mL vial. The molecular weight was confirmed by GPC as it can be seen in Figure S2(c). The ROP was used for polymerization of PLA. PS-OH6k (1g, 0.167mmol) was weighed and added to a 50mL vial along with DCM (3mL) and D,L-Lactide (1.944g, 13.49mmol). The mixture was well mixed and moved to a Schrenk flask. The flask was argon purged for 30 minutes and 1,8-Diazabicyclo(5.4.0)undec-7-ene (0.0254g, 0.167mmol) as catalyst for the reaction. The ROP reaction was left to go on for 3 hours and benzoic acid (0.0203g, 0.167mmol) was added to quench the reaction. The reaction mixture was stirred for another 10 minutes and was precipitated into methanol. The resulting PS-*b*-PLA BCP was dried in a vacuum

oven for two full days. The molecular weight was confirmed by GPC (Figure S2(c)), and its PS to PLA ratio was confirmed by NMR in Figure S1(c).

### Synthesis of Miktoarm Block Copolymers



**Figure S3.** <sup>1</sup>H-NMR spectrum of miktoarm PS-*b*-PLA BCPs, (a) MSL12-5, (b) MSL9-4, and (c) MSL6-7.

### Synthesis of miktoarm (PS)<sub>4</sub>-(PLA)<sub>4</sub> BCP (MSL9-4)

Styrene and THF was distilled into pre-heated burette and round bottom flask respectively before being used to synthesize polystyrene. Round bottom flasks containing purified styrene, THF were connected to the reactor as well as the argon purge line and the thermocouple. The reactor was heated with a heat gun and backfilled with argon three times. Dry ice-acetone bath was set up in order to create a -78°C environment. THF was introduced into the reactor which was placed

inside the dry ice-acetone bath. After temperature of THF became stable at  $-78^{\circ}\text{C}$ , *s*-BuLi (0.4365mL) was injected into the reactor through a septum connected to the reactor. After addition, the mixture showed a light yellow color. Styrene (5.5g, 52.80 mmol) was then added dropwise into the reactor. Upon one drop of styrene addition, the reaction mixture turned to a bright orange color. After all of the styrene was added, the polymerization was left to go on for an hour. Argon purged syringe was used to sample the linear polystyrene before addition of end capping agent. 2,4,6,8-Tetramethyl-2,4,6,8-tetrakis(propyl glycidyl ether)cyclotetrasiloxane (0.1065g, 0.1528mmol) was again added to the reactor through the septum. The reaction slowly turned light yellow over period of 20 minutes as polystyrene was end-capped forming a 4-arm star polystyrene (Star-PS9k,  $M_{n, PS} = 9.0 \text{ kg/mol}$ ). The reaction was terminated using 5mL of methanol which upon addition, turned into clear color. The reaction mixture was precipitated by pouring the reaction mixture into a beaker containing 3L of methanol. Polymer precipitate was collected and dried in a vacuum oven for 2 days. The molecular weights of linear and miktoarm polymers were taken by GPC as shown in Figure 2(b). Synthesized Star-PS9k (1g, 0.028mmol) was weighed and put into a 50mL vial along with D,L-Lactide (0.556g, 3.854mmol) and DCM (3mL). The mixture was well stirred and put into a Schrenk flask. The mixture was then purged with argon for 30 minutes. While stirring, DBU (4.229g, 0.028mmol) was put into the mixture using a argon purged syringe needle. The reaction was left to go on for 24 hours. Benzoic acid (3.392mg, 0.028mmol) was added to the reaction mixture and was left to be stirred for another 5 minutes. The mixture was then precipitated dropwise into methanol. The polymer precipitate was collected and dried in a vacuum oven for 2 days. GPC profile and NMR results for the synthesized miktoarm polymer are shown in Figure 2(b) and Figure S3(b), respectively.

### Synthesis of miktoarm (PS)<sub>4</sub>-(PLA)<sub>4</sub> BCP (MSL6-7)

Styrene and THF was distilled into pre-heated burette and round bottom flask respectively before being used to synthesize polystyrene. Round bottom flasks containing purified styrene, THF were connected to the reactor as well as the argon purge line and the thermocouple. The reactor was heated with a heat gun and backfilled with argon three times. Dry ice-acetone bath was set up in order to create a -78°C environment. THF was introduced into the reactor which was placed inside the dry ice-acetone bath. After temperature of THF became stable at -78°C, *s*-BuLi (0.6548mL) was injected into the reactor through a septum connected to the reactor. After addition, the mixture showed a light yellow color. Styrene (5.5g, 52.80 mmol) was then added dropwise into the reactor. Upon one drop of styrene addition, the reaction mixture turned to a bright orange color. After all of the styrene was added, the polymerization was left to go on for an hour. Argon purged syringe was used to sample the linear polystyrene before addition of end capping agent. 2,4,6,8-Tetramethyl-2,4,6,8-tetrakis(propyl glycidyl ether)cyclotetrasiloxane (0.1597g, 0.2292mmol) was again added to the reactor through the septum. The reaction slowly turned light yellow over period of 20 minutes as polystyrene was end-capped forming a 4-arm star polystyrene (Star-PS6k,  $M_{n, PS} = 6.0$  kg/mol). The reaction was terminated using 5mL of methanol which upon addition, turned into clear color. The reaction mixture was precipitated by pouring the reaction mixture into a beaker containing 3L of methanol. Polymer precipitate was collected and dried in a vacuum oven for 2 days. The molecular weights of linear and miktoarm polymers were taken by GPC as shown in Figure 2(c). Synthesized Star-PS6k (1g, 0.042mmol) was weighed and put into a 50mL vial along with D,L-Lactide (1.944g, 13.49mmol) and DCM (3mL).

The mixture was well stirred and put into a Schrenk flask. The mixture was then purged with argon for 30 minutes. While stirring, DBU (6.343mg, 0.042mmol) was put into the mixture using a argon purged syringe needle. The reaction was left to go on for 24 hours. Benzoic acid (5.088mg, 0.042mmol) was added to the reaction mixture and was left to be stirred for another 5 minutes. The mixture was then precipitated dropwise into methanol. The polymer precipitate was collected and dried in a vacuum oven for 2 days. GPC profile and NMR results for the synthesized mikroarm polymer are shown in Figure 2(c) and Figure S3(c), respectively.