

Successive Synthesis of Miktoarm Star Polymers Having up to Seven Arms by a New Iterative Methodology Based on Living Anionic Polymerization Using a Trifunctional Lithium Reagent

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The Supporting Information

Synthesis of a 4-Arm ABCD μ -Star Polymer Composed of PCHMA, PMMA, PBnMA, and P(acetal-DIMA) Segments. TBDMS-PLi (0.168 mmol) was first end-capped with styrene (0.730 mmol) in the presence of TMEDA (0.486 mmol) in *tert*-butylbenzene (3.57 mL) at 0 °C for 15 min, followed by in-situ reacting with **2** (0.237 mmol) in THF (8.25 mL) at -78 °C for 15 min. Thus, a new trifunctional lithium

reagent, **3**, substituted with trimethylsilyl (TMS), *tert*-butyldimethylsilyl (TBDMS), and tetrahydropyranyl (THP) ethers, was prepared. With the use of **3** as an anionic initiator, CHMA (7.93 mmol) in THF solution (6.90 mL) was polymerized at -78 °C for 2.5 h. Prior to the polymerization, LiCl (0.556 mmol) in THF solution (2.00 mL) was added to the polymerization system. After the polymerization was terminated with degassed methanol, the reaction mixture, after addition of a catalytic amount of K₂CO₃, was stirred for 15 min, and poured into a large amount of methanol to precipitate the polymer. The resulting polymer was reprecipitated from THF to methanol and freeze-dried from its absolute benzene solution. In the precipitation step, the TMS ether of **2** was selectively and completely deprotected to regenerate the hydroxyl group. Thus, a chain-end-(hydroxyl, TBDMS and THP ethers)-functionalized PCHMA was obtained in 95% yield (1.43 g). M_n (RALLS) = 11.2 kg/mol and M_w/M_n (SEC) = 1.05. ¹H NMR (CDCl₃) (300 MHz): δ = 7.24-6.21 (m, Ar), 4.66 (s, -O-CH-), 4.42 (s, Ar-CH₂-), 3.86, 3.45 (s, -CH₂- in THP), 2.33-0.65 (broad, backbone and -C(CH₃)₃), -0.02 (s, Si-(CH₃)₂).

Under an atmosphere of nitrogen, the chain-end-functionalized PCHMA (0.128 mmol for the hydroxyl functionality) dissolved in THF (20 mL) was mixed with PPh₃ (6.38 mmol), α -phenylacrylic acid (6.38 mmol), and diisopropyl azodicarboxylate (DIAD) (6.38 mmol) at 0 °C. The reaction mixture was allowed to react at 25 °C for 16

h and poured into methanol to precipitate the polymer. The polymer was purified by reprecipitation twice from THF solution to methanol and freeze-dried from its absolute benzene solution for 24 h. The polymer was obtained in 96% yield (1.37 g). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.21 (m, Ar), 6.31 and 5.87 (s, $\text{C}=\text{CH}_2$), 5.10 (s, Ar- CH_2 -OCO), 4.66 (s, -O-CH-), 4.42 (s, Ar- CH_2 -), 3.86, 3.45 (s, - CH_2 - in THP), 2.33-0.65 (broad, backbone and - $\text{C}(\text{CH}_3)_3$), -0.02 (s, Si-(CH_3)₂).

MMA (24.4 mmol) was polymerized at -78 °C for 20 min with the initiator prepared from *sec*-BuLi (0.233 mmol) and DPE (0.335 mmol) in the presence of LiCl (0.820 mmol) in THF solution (30.9 mL). The resulting living PMMA was in-situ reacted with the above PCHMA end-functionalized with PA, TBDMS ether, and THP ether (0.0710 mmol for the PA functionality) dissolved in dry THF (15.3 mL), precooled at -78 °C. The reaction mixture was allowed to further react at -40 °C for 20 h. The reaction was quenched with degassed methanol and polymers were precipitated in methanol. The target PCHMA-*block*-PMMA in-chain-functionalized with TBDMS and THP ethers was isolated in 93% yield by the fractional precipitation using benzene/methanol (1/5 (v/v)), and the isolated polymer was reprecipitated from THF to methanol and freeze-dried from its absolute benzene solution for 24 h (1.48 g, 93%). M_n (RALLS) = 22.2 kg/mol and M_w/M_n = 1.05 (SEC), ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.21 (m, Ar), 4.66 (s,

-O-CH-), 4.39 (s, Ar-CH₂-), 3.60 (s, -O-CH₃), 2.33-0.65 (broad, backbone and -C(CH₃)₃), -0.02 (s, Si-(CH₃)₂).

Under an atmosphere of nitrogen, the resulting PCHMA-*block*-PMMA in-chain-functionalized with TBDMS and THP ethers (0.0667 mmol for the TBDMS ether) dissolved in dry THF (15 mL) was mixed with (C₄H₉)₄NF (2.10 mmol) and phenol (2.10 mmol) in THF solution (2.10 mL) at 25 °C. The reaction mixture was allowed to stir at 25 °C for 16 h and then poured into a large amount of methanol to precipitate the polymer. The polymer was purified by reprecipitation from THF to methanol and freeze-dried from its absolute benzene solution (1.42 g, 96%). ¹H NMR (CDCl₃) (300 MHz): δ = 7.24-6.21 (m, Ar), 4.66 (s, -O-CH-), 4.39 (s, Ar-CH₂-), 3.60 (s, -O-CH₃), 2.33-0.65 (broad, backbone). Thus, the TBDMS ether was completely deprotected, while the THP ether remained unchanged under such conditions.

The resulting PCHMA-*block*-PMMA (0.0640 mmol for the hydroxyl group) was esterified with α -phenylacrylic acid in the same manner as that mentioned above. The polymer was purified by the reprecipitation three times from THF solution to methanol and freeze-dried from its absolute benzene solution for 24 h (1.40 g, 99%). ¹H NMR (CDCl₃) (300 MHz): δ = 7.24-6.21 (m, Ar), 6.19 and 5.80 (s, C=CH₂), 4.66 (s, -O-CH-), 4.39 (s, Ar-CH₂-), 3.60 (s, -O-CH₃), 2.33-0.65 (broad, backbone).

BnMA (7.55 mmol) was polymerized at -78 °C for 1 h with the initiator prepared from *sec*-BuLi (0.116 mmol) and DPE (0.147 mmol) in the presence of LiCl (0.387 mmol) in THF solution (13.3 mL). The resulting living PBnMA was in-situ reacted with the above in-chain-(PA and THP ether)-functionalized PCHMA-*block*-PMMA (0.0315 mmol for the PA functionality) at -40 °C for 20 h. After quenching with degassed methanol, the target 3-arm ABC μ -star was isolated in 85% yield (0.912 g) by SEC fractionation. M_n (RALLS) = 34.8 kg/mol and M_w/M_n = 1.03 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.21 (m, Ar), 4.89 (s, Ar- CH_2 -), 4.66 (s, -O- CH -), 3.60 (s, -O- CH_3), 2.33-0.53 (broad, backbone).

The resulting 3-arm ABC μ -star polymer core-functionalized with THP ether (0.0262 mmol for the THP ether) was dissolved in THF (9.00 mL) containing 10 drops of conc. HCl. The reaction mixture was allowed to stir at 25 °C for 16 h and then poured into a large amount of methanol to precipitate the polymer. The polymer was purified by reprecipitation from THF to methanol and freeze-dried from its absolute benzene solution (0.807 g, 88%). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.21 (m, Ar), 4.89 (s, Ar- CH_2 -), 4.66 (s, -O- CH -), 3.60 (s, -O- CH_3), 2.33-0.53 (broad, backbone).

The resulting 3-arm ABC μ -star core-functionalized with hydroxyl group (0.0231 mmol for the hydroxyl group) was esterified with α -phenylacrylic acid in the same

manner as that mentioned above. The reprecipitation three times from THF solution to methanol, followed by freeze-drying, gave the core-PA-functionalized 3-arm ABC μ -star polymer (0.720 g, 89%). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.21 (m, Ar), 6.31 and 5.87 (s, $\text{C}=\text{CH}_2$), 4.89 (s, $\text{Ar}-\text{CH}_2-$), 4.66 (s, $-\text{O}-\text{CH}-$), 3.60 (s, $-\text{O}-\text{CH}_3$), 2.33-0.53 (broad, backbone).

Acetal-DIMA (3.03 mmol) was polymerized at -78°C for 1 h with the initiator prepared from *sec*-BuLi (0.0739 mmol) and DPE (0.137 mmol) in the presence of LiCl (0.283 mmol) in THF solution (7.14 mL). After sampling of the living polymer to a certain extent, the residual living P(acetal-DIMA) (0.0139 mmol) was in-situ reacted with the above core-PA-functionalized 3-arm ABC μ -star (0.00431 mmol for the PA functionality) at -40°C for 20 h. After quenching the polymerization with degassed methanol, the target 4-arm ABCD μ -star was isolated in 83% yield (0.155 g) by the fractional precipitation using methanol. M_n (RALLS) = 43.2 kg/mol and M_w/M_n = 1.03 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.21 (m, Ar), 4.89 (s, $\text{Ar}-\text{CH}_2-$), 4.66 (s, $-\text{O}-\text{CH}-$), 4.39-3.67 (m, $-\text{CH}_2-\text{CH}-\text{CH}_2-$), 3.60 (s, $-\text{O}-\text{CH}_3$), 2.33-0.53 (broad, backbone).

Synthesis of a 4-Arm ABCD μ -Star Polymer Composed of PAMA, PS, PMOEMA, and P2VP Segments. The synthesis of the title 4-arm ABCD μ -star polymer was also carried out in the same manner as that mentioned before except for

the use of different living polymers. At first, AMA (14.5 mmol) was polymerized with **3** (0.0816 mmol) in the presence of LiCl (0.381 mmol) in THF solution (15.5 mL) at -78 °C for 7 h and the polymerization was terminated with degassed methanol. The polymer was precipitated in methanol. After the TMS ether was selectively deprotected by treatment with methanol containing K₂CO₃, the regenerated hydroxyl group was converted to the PA reaction site by the Mitsunobu esterification reaction with α -phenylacrylic acid. Thus, a chain-end-(PA, TBDMS and THP ether)-functionalized PAMA was prepared. M_n (RALLS) = 30.6 kg/mol and M_w/M_n = 1.02 (SEC). ¹H NMR (CDCl₃) (300 MHz): δ = 7.24-6.21 (m, Ar), 6.00-5.82 (m, -CH=CH₂), 5.40-5.20 (m, -CH=CH₂), 4.48 (s, -CH₂-CH=CH₂), 2.33-0.65 (broad, backbone and -C(CH₃)₃), -0.02 (s, Si-(CH₃)₂).

Styrene (15.5 mmol) was polymerized with *sec*-BuLi (0.0819 mmol) in THF solution (11.3 mL) at -78 °C for 1 h. Then, DPE (0.204 mmol) was added to end-cap the chain-end anion at -78 °C for 20 min prior to the linking reaction. After sampling the living PS end-capped with DPE to a certain extent, the residual living polymer (0.0350 mmol) was in-situ added to the above chain-end-(PA, TBDMS and THP ethers)-functionalized PAMA (0.0167 mmol for the PA functionality) dissolved in absolute THF solution (10.0 mL), precooled at -78 °C. The reaction was allowed to

further react at -78 °C for 12 h and quenched with degassed methanol. The polymer mixture was precipitated in a large excess of methanol, reprecipitated twice from THF to methanol, and freeze-dried from its absolute benzene solution. The target PAMA-*block*-PS in-chain-functionalized with TBDMS and THP ethers was isolated in 75% (0.630 g) yield by the fractional precipitation using benzene/cyclohexane/hexane (2/8/5 (v/v/v)). The isolated polymer was reprecipitated from THF to methanol and freeze-dried from its absolute benzene solution for 24h.

Deprotection of the TBDMS ether with (C₄H₉)₄NF in THF, followed by esterification reaction with α -phenylacrylic acid, was carried out in the same manners as those mentioned above. Thus, an in-chain-(PA and THP ether)-functionalized PAMA-*block*-PS was obtained in 86% yield (0.540 g). M_n (RALLS) = 50.3 kg/mol and M_w/M_n = 1.03 (SEC). ¹H NMR (CDCl₃) (300 MHz): δ = 7.24-6.21 (m, Ar), 6.00-5.82 (m, -CH=CH₂), 5.40-5.20 (m, -CH=CH₂), 4.48 (s, -CH₂-CH=CH₂), 2.33-0.58 (broad, backbone).

MOEMA (10.5 mmol) was polymerized at -78 °C for 2 h with the initiator prepared from *sec*-BuLi (0.0888 mmol) and DPE (0.132 mmol) in the presence of LiCl (0.458 mmol) in THF solution (16.7 mL). After sampling the resulting living PMOEMA to a certain extent, the residual living polymer (0.0356 mmol) was in-situ reacted with the

above in-chain-(PA and THP ether)-functionalized PAMA-*block*-PS (0.0107 mmol for the PA functionality) at -40 °C for 20 h. A 3-arm ABC μ -star polymer of the linked product was isolated in 71% yield (0.520 g) by the fractional precipitation using methanol.

After usual work up, the deprotection reaction of the THP ether with HCl, followed by esterification reaction with α -phenylacrylic acid, was carried out in the same manners as those mentioned above. Thus, a core-PA-functionalized 3-arm ABC μ -star polymer composed of PAMA, PS, and PMOEMA segments was obtained in 93% yield (0.484 g). M_n (RALLS) = 67.3 kg/mol and M_w/M_n = 1.03 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.21 (m, Ar), 6.00-5.82 (m, $-\text{CH}=\text{CH}_2$), 5.40-5.20 (m, $-\text{CH}=\text{CH}_2$), 4.48 (s, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 4.10 (s, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.59 (s, $-\text{CH}_2-\text{CH}_2-\text{OCH}_3$), 3.38 (s, $-\text{OCH}_3$), 2.33-0.58 (broad, backbone).

2VP (11.0 mmol) was polymerized at -78 °C for 30 min with the initiator prepared from *sec*-BuLi (0.0862 mmol) and DPE (0.156 mmol) in THF solution (11.3 mL). After sampling the resulting living P2VP to a certain extent, the residual living P2VP (0.0161 mmol) was in-situ reacted with the above core-PA-functionalized 3-arm ABC μ -star polymer (0.00728 mmol for the PA functionality) dissolved in THF solution (12.0 mL), precooled at -78 °C. The reaction was allowed to further react at -78 °C for 12 h and

quenched with degassed methanol. After the polymer mixture was precipitated in methanol, the target ABCD μ -star polymer was isolated in 78% yield by the fractional precipitation using benzene/ethanol/hexane (2/3/10 (v/v/v)). The isolated polymer was reprecipitated from THF to hexane twice and freeze-dried from its absolute benzene solution for 24 h (78%, 0.460 g). M_n (RALLS) = 80.0 kg/mol and M_w/M_n = 1.04 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 8.45-8.05 (m, $-\text{N}=\text{CH}-$), 7.24-6.14 (m, Ar), 6.00-5.82 (m, $-\text{CH}=\text{CH}_2$), 5.40-5.20 (m, $-\text{CH}=\text{CH}_2$), 4.48 (s, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 4.10 (s, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.59 (s, $-\text{CH}_2-\text{CH}_2-\text{OCH}_3$), 3.38 (s, $-\text{OCH}_3$), 2.46-0.58 (broad, backbone).

Successive Synthesis of μ -Star Polymers by a New Stepwise Iterative Methodology. The synthesis was started from the same chain-end-(PA, TBDMS and THP ethers)-functionalized PCHMA as that used for the synthesis of 4-arm ABCD μ -star polymer mentioned above. A living PS (0.0783 mmol) was reacted with the above functionalized PCHMA (0.0510 mmol for the PA functionality) dissolved in THF solution (12.0 mL), precooled at -78°C . The reaction was allowed to further react at -78°C for 12 h and terminated with degassed methanol. After usual work up, a PCHMA-*block*-PS in-chain-functionalized with TBDMS and THP ethers was isolated in 85% yield by SEC fractionation. Deprotection reaction of the TBS ether and the

subsequent esterification reaction with α -phenylacrylic acid were carried out in the same manners as those mentioned above. Thus, an in-chain-(PA and THP ether)-functionalized PCHMA-*block*-PS was obtained in 92% yield (0.857 g). M_n (RALLS) = 22.6 kg/mol and M_w/M_n = 1.04 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.18 (m, Ar), 6.21 and 5.80 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 2.33-0.49 (broad, backbone).

4MOS (9.71 mmol) in THF solution (9.98 mL) was polymerized at -78°C for 1 h with *sec*-BuLi (0.0819 mmol), followed by end-capping the resulting living P4MOS with DPE (0.215 mmol) at -78°C for 30 min prior to the linking reaction. After sampling the resulting living polymer to a certain extent, the residual living P4MOS end-capped with DPE (0.0658 mmol) was in-situ reacted with the above functionalized PCHMA-*block*-PS (0.0371 mmol for the PA functionality) in THF solution at -78°C . The reaction was allowed to further react at -78°C for 12 h and terminated with degassed methanol. After usual work up, a core-(THP ether)-functionalized 3-arm ABC μ -star polymer composed of PCHMA, PS, and P4MOS segments was isolated in 56% yield by fractional precipitation, followed by SEC fractionation. The THP ether at the core was deprotected with HCl and the regenerated hydroxyl group was subsequently converted to the PA reaction site in the same manners as those mentioned above. Thus, a

core-PA-functionalized ABC μ -star polymer was obtained in 87% yield (0.636 g). M_n (RALLS) = 34.9 kg/mol and $M_w/M_n = 1.03$ (SEC). ^1H NMR (CDCl_3) (300 MHz): $\delta =$ 7.24-6.18 (m, Ar), 6.31 and 5.87 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 3.74 (s, $-\text{OCH}_3$), 2.33-0.49 (broad, backbone).

The trifunctional lithium reagent, **3**, (0.0338 mmol) was prepared in the same manner and in-situ added to the core-PA-functionalized ABC μ -star polymer (0.0182 mmol for the PA functionality) dissolved in THF at -78°C . The reaction was allowed to react at -78°C for 12 h and then terminated with degassed methanol. After usual work up, the TMS ether was deprotected and the regenerated hydroxyl group was converted to the PA reaction site. Thus, a core-(PA, TBDMS and THP ethers)-functionalized ABC μ -star polymer was obtained in 86% yield (0.548 g). ^1H NMR (CDCl_3) (300 MHz): $\delta =$ 7.24-6.18 (m, Ar), 6.31 and 5.87 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 3.74 (s, $-\text{OCH}_3$), 2.33-0.49 (broad, backbone and $-\text{C}(\text{CH}_3)_3$), -0.02 (s, $\text{Si}-(\text{CH}_3)_2$).

A living P4MS was prepared by the polymerization of 4MS with *sec*-BuLi in THF at -78°C for 1 h. After end-capping the chain-end anion with DPE in THF at -78°C for 1 h, the resulting living polymer (0.0367 mmol) was in-situ reacted with the above core-functionalized ABC μ -star polymer (0.0157 mmol for the PA functionality) dissolved in THF at -78°C . The reaction was allowed to react at -78°C for 12 h and

quenched with degassed methanol. After usual work up, the target 4-arm ABCD μ -star polymer composed of PCHMA, PS, P4MOS, and P4MS segments was isolated in 83% yield by SEC fractionation. Deprotection of the TBDMS ether, followed by esterification reaction of the regenerated hydroxyl group with α -phenylacrylic acid, was similarly carried out as above. Thus, a core-(PA and THP ether)-functionalized 4-arm ABCD μ -star polymer was obtained in 86% yield (0.518 g). M_n (RALLS) = 47.1 kg/mol and M_w/M_n = 1.03 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.18 (m, Ar), 6.21 and 5.80 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 3.74 (s, $-\text{OCH}_3$), 2.33-0.49 (broad, backbone), 2.27 (s, $-\text{C}_6\text{H}_4-\text{CH}_3$).

A living PMMA (0.0350 mmol) was prepared by the polymerization of MMA with the initiator from *sec*-BuLi and DPE in THF at -78°C for 1 h and in-situ reacted with the above core-PA-functionalized 4-arm ABCD μ -star polymer (0.0110 mmol for the PA functionality) in THF solution at -78°C . The reaction was allowed to react at -40°C for 20 h and quenched with degassed methanol. After usual work up, a 5-arm ABCDE μ -star polymer composed of PCHMA, PS, P4MOS, P4MS, and PMMA segments was isolated in 82% yield by the fractional precipitation using benzene/methanol (1/5 (v/v)). The THP ether was deprotected with HCl and the regenerated hydroxyl group was converted to the PA function by the Mitsunobu esterification reaction with

α -phenylacrylic acid. Thus, a core-PA-functionalized 5-arm ABCDE μ -star was prepared in 85% yield (0.432 g). M_n (RALLS) = 53.5 kg/mol and M_w/M_n = 1.04 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.18 (m, Ar), 5.87 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 3.74 (s, $\text{Ar}-\text{OCH}_3$), 3.60 (s, COOCH_3), 2.33-0.49 (broad, backbone), 2.27 (s, $-\text{C}_6\text{H}_4-\text{CH}_3$).

The trifunctional lithium reagent, **3**, (0.0319 mmol) was reacted with the above core-PA-functionalized ABCDE μ -star (0.00807 mmol for the PA functionality) at -78°C for 12 h and the reaction was then quenched with degassed methanol. After usual work up, the TMS ether was converted to the PA reaction site via the deprotection and the subsequent esterification. Thus, a core-(PA, TBDMS and THP ethers)-functionalized 5-arm ABCDE μ -star polymer was obtained in 75% yield (0.323 g). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.18 (m, Ar), 5.84 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 3.74 (s, $\text{Ar}-\text{OCH}_3$), 3.60 (s, COOCH_3), 2.33-0.49 (broad, backbone and $-\text{C}(\text{CH}_3)_3$), 2.27 (s, $-\text{C}_6\text{H}_4-\text{CH}_3$), -0.02 (s, $\text{Si}-(\text{CH}_3)_2$).

A living PEMA was prepared by the polymerization of EMA with the initiator from *sec*-BuLi and DPE in THF at -78°C for 1 h and the resulting living PEMA (0.0200 mmol) was in-situ reacted with the above 5-arm ABCDE μ -star (0.00604 mmol for the PA functionality) in THF at -78°C . The reaction was allowed to further react at -40°C

for 20 h and quenched with degassed methanol. After usual work up, a 6-arm ABCDEF μ -star polymer composed of PCHMA, PS, P4MOS, P4MS, PMMA, and PEMA arms was isolated in 84% yield by the fractional precipitation using benzene/methanol (1/10 (v/v)). The TBDMS ether was then converted to the PA reaction site, via the deprotection and the subsequent esterification reaction by same procedures as those mentioned above. Thus, a core (PA and THP ether)-functionalized 6-arm ABCDEF μ -star polymer was prepared in 77% yield (0.244 g). M_n (RALLS) = 64.9 kg/mol and M_w/M_n = 1.05 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.18 (m, Ar), 5.80 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 4.14-3.98 (m, $-\text{O}-\text{CH}_2-\text{CH}_3$) 3.74 (s, $\text{Ar}-\text{OCH}_3$), 3.60 (s, COOCH_3), 2.33-0.49 (broad, backbone), 2.27 (s, $-\text{C}_6\text{H}_4-\text{CH}_3$).

A living PMOEMA (0.0130 mmol) was prepared by the polymerization of MOEMA with the initiator from *sec*-BuLi and DPE in THF at -78°C for 1 h and in-situ reacted with the above functionalized ABCDEF μ -star polymer (0.00376 mmol for the PA functionality) in THF at -78°C . The reaction was allowed to further react at -40°C for 20 h and quenched with degassed methanol. After usual work up, a core-(THP ether)-functionalized 7-arm ABCDEFG μ -star polymer composed of PCHMA, PS, P4MOS, P4MS, PMMA, PEMA, and PMOEMA arms was isolated in 62% yield by the fractional precipitation using benzene/methanol (1/20 (v/v)). The polymer was

reprecipitated from THF to methanol twice and freeze-dried from its absolute benzene solution (0.151 g, 62%). M_n (RALLS) = 74.2 kg/mol and M_w/M_n = 1.04 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.24-6.18 (m, Ar), 5.80 (s, $-\text{CH}=\text{CH}_2$), 4.66 (s, $-\text{O}-\text{CH}-$), 4.18-3.98 (m, $-\text{O}-\text{CH}_2-\text{CH}_3$, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_3$) 3.74 (s, $\text{Ar}-\text{OCH}_3$), 3.60 (s, COOCH_3 , $-\text{CH}_2-\text{OCH}_3$), 3.38 (s, $-\text{CH}_2-\text{OCH}_3$), 2.33-0.49 (broad, backbone), 2.27 (s, $-\text{C}_6\text{H}_4-\text{CH}_3$).

Synthesis of a 6-Arm $\text{A}_2\text{B}_2\text{C}_2$ μ -Star Polymer. The target polymer was synthesized by the reaction of 1,4-dilithio-1,1,4,4-tetraphenylbutane with a core-PA-functionalized 3-arm ABC μ -star polymer composed of PMMA, P α MS, and PMOEMA segments in THF at -78°C in a titration manner. The above core-PA-functionalized 3-arm ABC μ -star polymer was prepared in similar manners to those used for the synthesis of other core-PA-functionalized 3-arm ABC μ -star polymers mentioned above. M_n (RALLS) = 28.7 kg/mol and M_w/M_n = 1.04 (SEC). ^1H NMR (CDCl_3) (300 MHz): δ = 7.49-6.35 (m, Ar), 6.31 and 5.87 (s, $\text{C}=\text{CH}_2$), 4.10 (s, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 3.59 (s, $-\text{CH}_2-\text{CH}_2-\text{OCH}_3$, COOCH_3), 3.38 (s, $-\text{CH}_2-\text{OCH}_3$), 2.46-0.06 (broad, backbone).

Lithium naphthalenide (0.0754 mmol) and DPE (0.138 mmol) were mixed in THF (4.87 mmol) at -78°C and the reaction mixture was allowed to stir for 30 min at -78°C . The deep red colored solution was in-situ added slowly to the above core-PA-functionalized 3-arm ABC μ -star polymer (0.460 g, 0.0160 mmol for the PA

functionality) in THF (10 mL) at -78 °C until the red color remained in the reaction system and the reaction mixture was allowed to react at -78 °C for 12 h. Although the red color still remained after 12 h, the reaction was quenched with degassed methanol and the polymer mixture was precipitated in methanol. After usual work up, the target A₂B₂C₂ μ-star polymer was isolated in 50% yield (0.230 g) by SEC fractionation. The isolated polymer was reprecipitated in methanol twice and freeze-dried from its absolute benzene solution. M_n (RALLS) = 58.0 kg/mol and M_w/M_n = 1.03 (SEC). ¹H NMR (CDCl₃) (300 MHz): δ = 7.49-6.35 (m, Ar), 4.10 (s, -O-CH₂-CH₂-), 3.59 (s, -CH₂-CH₂-OCH₃, COOCH₃), 3.38 (s, -CH₂-OCH₃), 2.46-0.65 (broad, backbone), 0.65-0.02 (m, α -CH₃-C-C₆H₅).