Supporting Information

Facile Synthesis of Multiarmed and Multicomponent Star Polymers by New Iterative Methodology Using (Formyl-Protected 1,3-Dioxolane)-End-Functionalized Polymer Anions

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Experimental details

General Synthetic Procedure for μ-Star Polymers. Except for deprotection and esterification reactions, all of the polymerizations and linking reactions were carried out under high vacuum conditions (10^{-6} torr) in sealed handmade glass reactors equipped with breakseals. The operations were performed according to the usual high vacuum technique with breakseals previously reported.[1]

The typical synthetic procedures are described in the following sections. An excess amount (1.5- – 3-fold excess) of the living anionic polymer for the formyl or PA reaction site was usually used. In general, yields of the objective polymers were quantitative. The synthesized μ-star polymers were isolated by fractional precipitation (yield: ca. 40 ~ 70%) or SEC fractionation (yield: ca. 60 ~ 80%). These polymers were purified by reprecipitation twice and freeze-dried for overnight, and measured by ^{1}H NMR, SEC, and RALLS.

Synthesis of 1,1-Bis(3-(1,3-dioxolan-2-yl)phenyl)ethylene (4). 1,1-di(3-formylphenyl)ethanol (22.4 g, 88.1 mmol)[2], ethylene glycol (12.2 g, 187 mmol), and a catalytic amount of *p*-toluene sulfonic acid were dissolved in toluene (100 mL) in 300 mL two-necked flask equipped with Dean-Stark head and the mixture was refluxed for 4.5 h. During refluxing, water was removed several times to shift the equilibrium. The reaction was then quenched with aqueous $NaHCO_3$ and the organic layer was washed with water and dried over $MgSO_4$. A small amount of K_2CO_3 was added to the organic layer to keep alkaline conditions. After filtration and evaporation, the residual oil was purified by column chromatography on silica using dichloromethane/hexane (1/1, vol/vol) as an eluent to yield **4** in 58% yield (16.5 g, 108 mmol). Finally, after the addition of a small amount of BuLi to **4** until a red color was appeared, the **4** was distilled on the high vacuum line (~ 10^{-6} torr) into the ampoules equipped with break-seals. ^{1}H NMR ($CDCl_3$): δ 7.77−7.21 (m, 8H, Ar), 5.70 (s, 2H, Ar−C*H*−O−), 5.40 (s, 2H, CH_2=C-Ar), 3.89 (m, 4H, -O-CH_2CH_2-O-), ^{13}C NMR ($CDCl_3$): δ 149.2, 141.7, 136.2, 128.7, 128.0, 125.7, 124.9, 114.7, 103.3, 64.9.

Synthesis of In-Chain-(OH and DOL)-Functionalized PMMA-*b*-PS. The chain-end-formyl-functionalized PMMA was prepared by the living anionic polymerization of MMA (17.3 mmol) with the initiator prepared from *sec*-BuLi (0.156 mmol) and **3** (0.188 mmol) in the presence LiCl (0.486 mmol). The deprotection the DOL was performed in the same manner as that reported in our previous paper[3]. M_n (SEC) = 13.6 kg mol^{-1}). ^{1}H NMR ($CDCl_3$): δ 9.86 (s, -C*H*O), 7.32−6.73 (br, aromatic), 3.81−3.53 (m, −COO-CH_3), 2.23−1.74 (br, −CH_2−C(CH_3)−), 1.21-0.84 (m, −CH_2−C(CH_3)−).

The resulting chain-end-formyl-functionalized PMMA (13.6 kg mol^{-1}, 0.0669 mmol) dissolved in dry THF (9.60 mL) was cooled to -78 °C and reacted with the living polystyrene end-capped with **3** (0.0842 mmol) in THF (12.2 mL) at -78 °C for 12 h. After quenching with degassed methanol, the reaction mixture was poured into methanol. Then, the objective in-chain-(OH and DOL)-functionalized PMMA-*b*-PS was isolated in 55% by fractional precipitation using diethyl ether/THF/hexane (200/60/100, vol/vol/vol). The isolated polymer was purified by reprecipitation from THF to methanol twice and freeze-dried from its absolute benzene solution (0.992 g, 0.0366 mmol for the hydroxyl function). ^{1}H NMR ($CDCl_3$): δ 7.31−6.45 (br, aromatic), 5.76 (d, -O-C*H*(Ar)-O-), 5.55 (s, -C-C*H*(Ar)-OH), 4.09 and 4.02 (d, -O-CH_2-CH_2-O-), 3.81-3.50 (m, -COO-CH_3), 2.61-0.77 (br, backbone). M_n (SEC) = 26.8 kg/mol.

Synthesis of Core-DOL-Functionalized 3-Arm ABC μ-Star Polymer. Under an atmosphere of nitrogen, a dry CH_2Cl_2 (5.0 mL) solution of α-phenylacryloyl chloride (0.420 g, 2.52 mmol) was added dropwise to a mixture of the in-chain-(OH and DOL)-functionalized PMMA-*b*-PS (0.980 g, 0.0361 mmol, M_n (SEC-RALLS) = 26.8 kg mol^{-1}) and DMAP (0.380 g, 3.12 mmol) in dry CH_2Cl_2 (15.0 mL) at 0 °C. The reaction mixture was warmed to 40 °C (reflux temperature) and allowed to stir for 12 h. The polymer was precipitated in methanol, reprecipitation twice from the THF solution to methanol, and freeze-dried from its absolute benzene solution. An in-chain-(PA and DOL)-functionalized PMMA-*b*-PS was obtained (0.870 g, 0.0321 mmol). ^{1}H NMR ($CDCl_3$): δ 7.32−6.40 (br, aromatic), 6.15 (s, CH_2=C(Ph)-COO-), 5.75 (d, -O−C*H*(Ar)−O−), 5.70 (s, CH_2=C(Ph)-COO-), 4.07 and 3.99 (d, -O-CH_2-CH_2-O-), 3.82−3.50 (m, -COO-CH_3), 2.61-0.77 (br, backbone).

The in-chain-(PA and DOL)-functionalized PMMA-*b*-PS (0.859 g, 0.0317 mmol) in THF (9.8 mL), precooled at -78 °C, was added to the living PBnMA (0.0102 mmol, M_n (SEC) = 10.7 kg mol^{-1}) in THF (10.8 mL) at -78 °C. The reaction mixture was then allowed to stand at -40 °C for 12 h. The reaction was terminated with a few drops of degassed methanol and the polymer mixture was precipitated in methanol. The linked product was isolated in 64% by SEC fractionation. The isolated polymer was reprecipitated twice from THF solution to methanol and freeze-dried from its absolute benzene solution. The target core-DOL-functionalized 3-arm ABC μ-star polymer was obtained (0.770 g, 64%). ^{1}H NMR ($CDCl_3$): δ 7.32−6.40 (br, aromatic), 5.75 (d, -O−C*H*(Ar)−O−), 5.01−4.80 (m, −CH_2−Ar), 4.03 (d, -OCH_2-CH_2-O-), 3.83−3.49 (m, -COO-CH_3), 2.62-0.77 (br, backbone). M_n (RALLS) = 37.8 kg/mol.

Synthesis of 5-Arm ABCDE μ-Star Polymer. The title 5-arm μ-star polymer was synthesized from the core-DOL-functionalized 3-arm ABC μ-star polymer by repeating the reaction sequence similar to the above-mentioned procedures. The reaction sequence involves deprotection of the DOL function to regenerate the formyl group (M_n = 37.8 kg mol^{-1}, 0.680 g (0.0182 mmol)), followed by the linking reaction of the living PαMS end-capped with **3** (M_n = 10.9 kg mol^{-1}, 0.0382 mmol). The usual work-up gave a 4-arm ABCD μ-star polymer core-functionalized with hydroxyl and DOL groups (yield 46%). ^{1}H NMR ($CDCl_3$): δ 7.49−6.36 (br, aromatic), 5.74 (d, -O−C*H*(Ar)−O−), 5.53 (s, -C-C*H*(Ar)-OH), 5.02−4.81 (m, −CH_2−Ar), 4.02 (d, -OCH_2-CH_2-O-), 3.83−3.48 (m, -COO-CH_3), 2.62-0.77 (br, backbone) , 0.66-0.03 (m, α-CH_3-C-Ar). M_n (RALLS) = 47.7 kg/mol.

The obtained 4-arm ABCD μ-star polymer (M_n = 47.7 kg mol^{-1}, 0.390 g, 0.00818 mmol) was esterified with α-phenylacryloyl chloride (0.120 g (0.720 mmol)), and DMAP (0.100 g (0.820 mmol)) in CH_2Cl_2 (20 mL) under the above-mentioned conditions. The same work-up gave a core-(PA and DOL)-functionalized 4-arm ABCD μ-star polymer composed of PMMA, PS, PBnMA, and PαMS arms (0.260 g, 0.00545 mmol, 67%). ^{1}H NMR ($CDCl_3$): δ 7.48−6.37 (br, aromatic), 6.15 (s, CH_2=C(Ph)-COO-), 5.74 (d, -O−C*H*(Ar)−O−), 5.69 (s, CH_2=C(Ph)-COO-), 5.02−4.82 (m, −CH_2−Ar), 4.04

(d, -OCH_2-CH_2-O-), 3.82−3.48 (m, -COO-CH_3), 2.63-0.76 (br, backbone) , 0.66-0.03 (m, α-CH_3-C-Ar). M_n (RALLS) = 47.6 kg mol^{-1}.

The living P2VP was prepared by the polymerization of 2VP (0.314 g, 2.99 mmol) with 1,1-diphenylhexyllithium (0.0273 mmol) in THF (10.2 mL) at -78 ^oC for 0.5 h and in-situ reacted with the core-(PA and DOL)-functionalized ABCD μ-star polymer (M_n = 47.6 kg mol^{-1}, 0.00263 mmol) in THF (5.62 mL) at -78 °C for 12 h. The usual work-up gave a target 5-arm ABCDE μ-star polymer, which was isolated in 53% yield by precipitation to methanol. ^{1}H NMR ($CDCl_3$): δ 8.45-8.04 (m, -N=C*H*-), 7.49−6.22 (br, aromatic), 5.76 (d, -O−C*H*(Ar)−O−), 5.02−4.83 (m, −CH_2−Ar), 4.05 (d, -OCH_2-CH_2-O-), 3.83−3.48 (m, -COO-CH_3), 2.65-0.76 (br, backbone) , 0.66-0.02 (m, α-CH_3-C-Ar). M_n (RALLS) = 56.2 kg mol^{-1}.

The other 5-arm ABCDE' μ-star polymer was similarly synthesized by the linking reaction of the living PCPPHM (M_n = 8.60 kg mol^{-1}, 0.0670 g, 0.00783 mmol) with the above-synthesized core-(PA and DOL)-functionalized ABCD μ-star polymer (M_n = 47.6 kg mol^{-1}, 0.124 g, 0.00261 mmol). ^{1}H NMR ($CDCl_3$): δ 7.82−6.37 (br, aromatic), 5.75 (d, -O−C*H*(Ar)−O−), 5.03−4.84 (m, −CH_2−Ar), 4.05-3.92 (m, -OCH_2-CH_2-O-, -COO-CH_2-CH_2-), 3.83−3.48 (m, -COO-CH_3), 2.65-0.76 (br, backbone) , 0.66-0.01 (m, α-CH_3-C-Ar). M_n (RALLS) = 57.2 kg/mol.

Synthesis of 5-Arm ABCDE μ-Star Polymer Composed of PMOS, PMS, PS, PαMS, and PTBSOS. The title 5-arm ABCDE μ-star polymer was synthesized by repeating the same reaction sequence under the conditions similar to those already mentioned. The NMR spectra of all the polymers were as follows: ^{1}H NMR, chain-end-formyl-functionalized PMOS: δ 9.86 (s, -CHO), 7.24−6.10 (br, aromatic), 3.86 (m, -O-CH_3), 2.21−0.64 (br, backbone and *sec*-Bu), in-chain-(OH and DOL)-functionalized PMOS-*b*-PMS: 7.22−6.12 (br, aromatic), 5.74 (d, -O−CH(Ar)−O−), 5.53 (s, -C-CH(Ar)-OH), 4.02 (d, -OCH_2-CH_2-O-), 3.86 (m, -O-CH_3), 2.28 (m, -Ph-CH_3) 2.62-0.77 (br, backbone), core-DOL-functionalized 3-arm ABC μ-star polymer: 7.23−6.09 (br, aromatic), 5.75 (d, -O−CH(Ar)−O−), 4.03 (d, -OCH_2-CH_2-O-), 3.87 (m, -O-CH_3), 2.29 (m, -Ph-CH_3) 2.62-0.76 (br, backbone), core-(OH and DOL)-functionalized 4-arm ABCD μ-star polymer: 7.24−6.08 (br, aromatic), 5.75 (d, -O−CH(Ar)−O−), 4.01 (d, -OCH_2-CH_2-O-), 3.86 (m, -O-CH_3), 2.30 (m, -Ph-CH_3) 2.62-0.76 (br, backbone), 0.67-0.09 (m, □-CH_3-C-Ar), core-DOL-functionalized 5-arm ABCDE μ-star polymer: 7.26−6.02 (br, aromatic), 5.75 (d, -O−CH(Ar)−O−), 4.01 (d, -OCH_2-CH_2-O-), 3.88 (m, -O-CH_3), 2.30 (m, -Ph-CH_3) 2.62-0.76 (br, backbone), 0.90 (s, -Si-^{t}Bu), 0.66-0.09 (m, α-CH_3-C-Ar), 0.01 (s, -Si-(CH_3)$_3$).

Synthesis of 7-Arm ABCD$_2$E$_2$ μ-Star Polymers. The 7-arm ABCD$_2$E$_2$ μ-star polymers were synthesized by repeating the same reaction sequence under the conditions similar to those already mentioned. The NMR spectra of all the polymers were as follows: ^{1}H NMR, chain-end-formyl-functionalized PS: 9.85 (s, -CHO), 7.24−6.09 (br, aromatic), 2.21−0.54 (br, backbone and *sec*-Bu), in-chain-(OH and DOL)-functionalized PS-*b*-PMS: 7.20−6.02 (br, aromatic), 5.77 (d, -O−CH(Ar)−O−), 4.02 (d, -OCH_2-CH_2-O-), 2.30 (m, -Ph-CH_3) 2.22-0.43 (br, backbone and *sec*-Bu), core-(DOL)$_2$-functionalized 3-arm ABC μ-star polymer: 7.21−6.00 (br, aromatic), 5.74 (d, -O−CH(Ar)−O−), 4.02 (d, -OCH_2-CH_2-O-), 2.29 (m, -Ph-CH_3), 2.24-0.77 (br, backbone), 0.66-0.09 (m, α-CH_3-C-Ar), core-((DOL)$_2$ and (OH)$_2$)-functionalized 5-arm ABCD$_2$ μ-star polymer: 7.22−6.01 (br, aromatic), 5.73 (d, -O−CH(Ar)−O−), 4.03 (d, -OCH_2-CH_2-O-), 3.85 (m, -O-CH_3), 2.30 (m, -Ph-CH_3), 2.25-0.76 (br, backbone), 0.65-0.07 (m, α-CH_3-C-Ar), core-(DOL)$_4$-functionlized 7-arm ABCD$_2$E$_2$ μ-star polymer: 7.21−6.00 (br, aromatic), 5.74 (d, -O−CH(Ar)−O−), 5.14 (s, vinyl proton (1,4-PIsp)), 4.76 and 4.69 (s, vinyl proton (3,4-PIsp)), 4.03 (d, -OCH_2-CH_2-O-), 3.86 (m, -O-CH_3), 2.31 (m, -Ph-CH_3), 2.25-0.76 (br, backbone), 0.65-0.06 (m, α-CH_3-C-Ar).

Synthesis of 9-Arm A$_3$B$_2$C$_4$ μ-Star Polymers. The title 9-arm A$_3$B$_2$C$_4$ μ-star polymer was synthesized by the iterative methodology using **4** described in the text. The NMR spectra of all the synthesized polymers were as follows: ^{1}H NMR, chain-end-(formyl)$_2$-functionalized PS: 10.1 (s, -CHO), 7.24−6.36 (br, aromatic), 2.21−0.54 (br, backbone and *sec*-Bu), in-chain-((OH)$_2$ and (DOL)$_4$)-functionalized 3-arm A$_3$ PSs: 7.23−6.33 (br, aromatic), 5.76 (d, -O−CH(Ar)−O−), 3.96 (d, -OCH_2-CH_2-O-), 2.22-0.45 (br, backbone and *sec*-Bu), core-(DOL)$_4$-functionalized 5-arm A$_3$B$_2$ μ-star polymer: 7.21−6.33 (br, aromatic), 5.74 (d, -O−CH(Ar)−O−), 3.98 (d, -OCH_2-CH_2-O-), 3.81−3.53 (m, −COO-CH_3), 2.23-0.84 (br, backbone and *sec*-Bu), core-(DOL)$_4$-functionalized 5-arm A$_3$B’$_2$ μ-star polymer: 7.83−6.32 (br, aromatic), 5.75 (d, -O−CH(Ar)−O−), 5.02-4.83 (m, −CH_2−Ar), 4.04-3.91 (m, -OCH_2-CH_2-O-, -COO-CH_2-CH$_2$-), 2.14-0.77 (br, backbone and *sec*-Bu), core-((DOL)$_8$ and (OH)$_4$)-functionalized 9-arm A$_3$B$_2$C$_4$ μ-star polymer: 7.22−6.01 (br, aromatic), 5.73 (d, -O−CH(Ar)−O−), 4.03 (d, -OCH_2-CH_2-O-), 3.85 (m, -O-CH_3), 2.30 (m, -Ph-CH_3), 2.25-0.76 (br, backbone), 0.65-0.07 (m, α-CH_3-C-Ar).

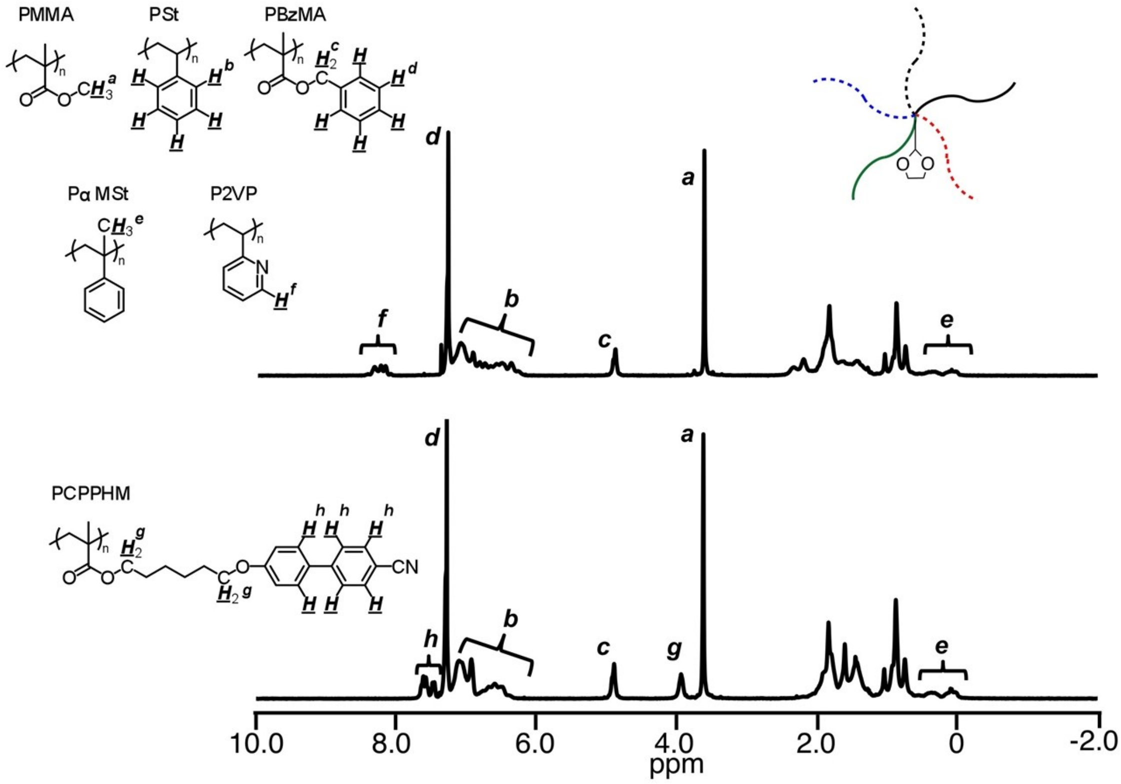


Fig S1. ^{1}H NMR spectra of the ABCDE and ABCDE’ μ-star polymers.

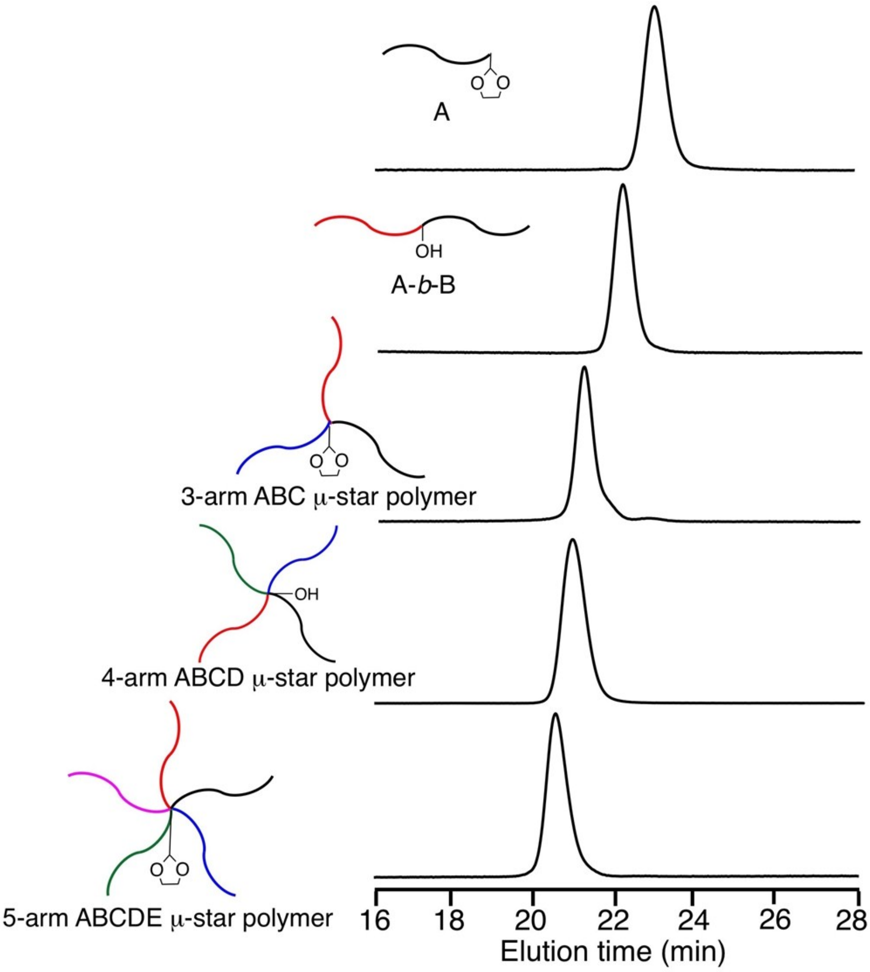


Fig S2. SEC profiles from A, AB, 3-arm ABC, 4-arm ABCD, to 5-arm ABCDE μ-star polymer composed of all PS derivatives.

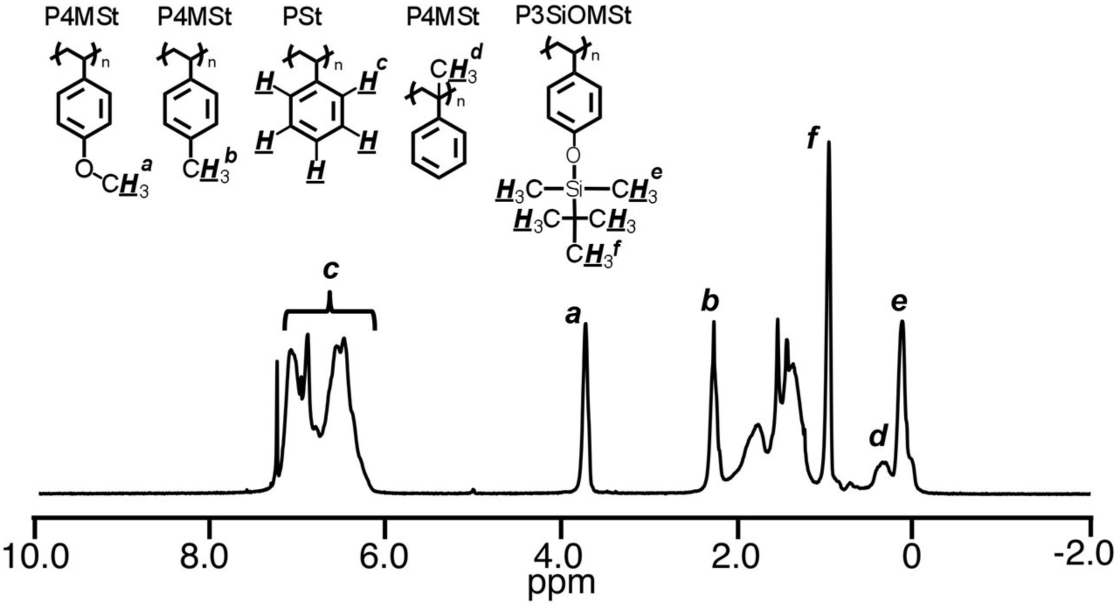


Fig S3. ^{1}H NMR spectrum of the ABCDE μ-star polymer composed of all polystyrene derivatives.

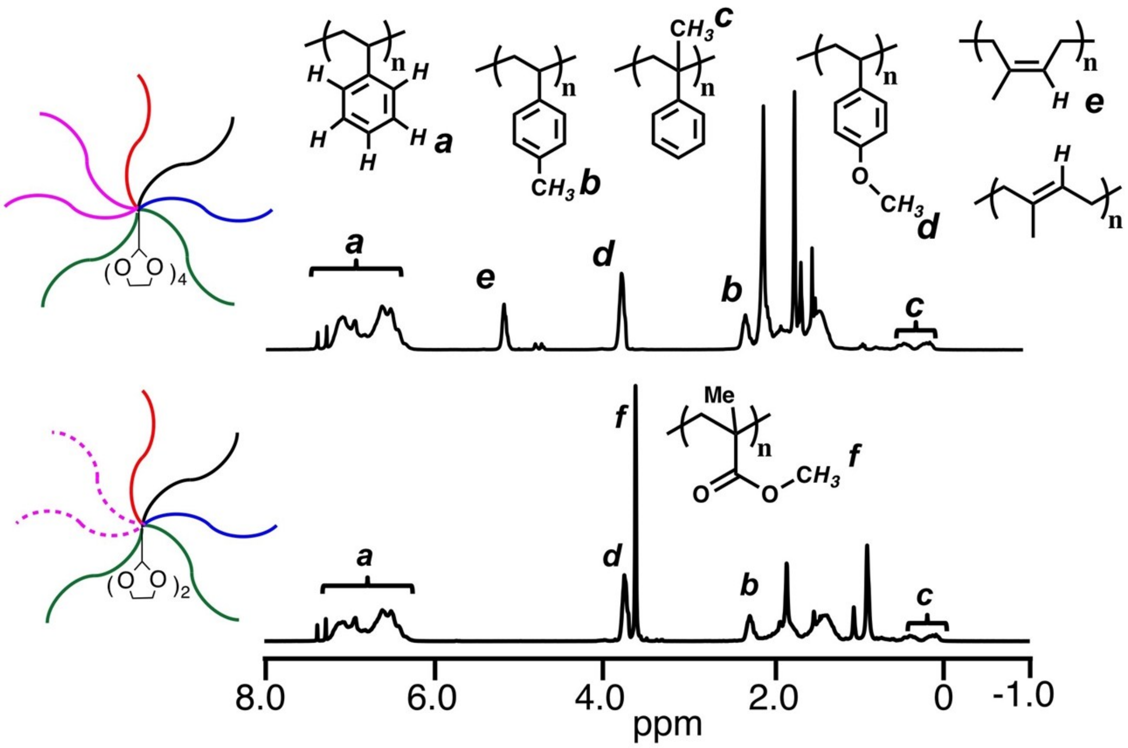


Fig S4. ^{1}H NMR spectra of the $ABCD_2E_2$ and $ABCD_2E'_2$ μ-star polymers.

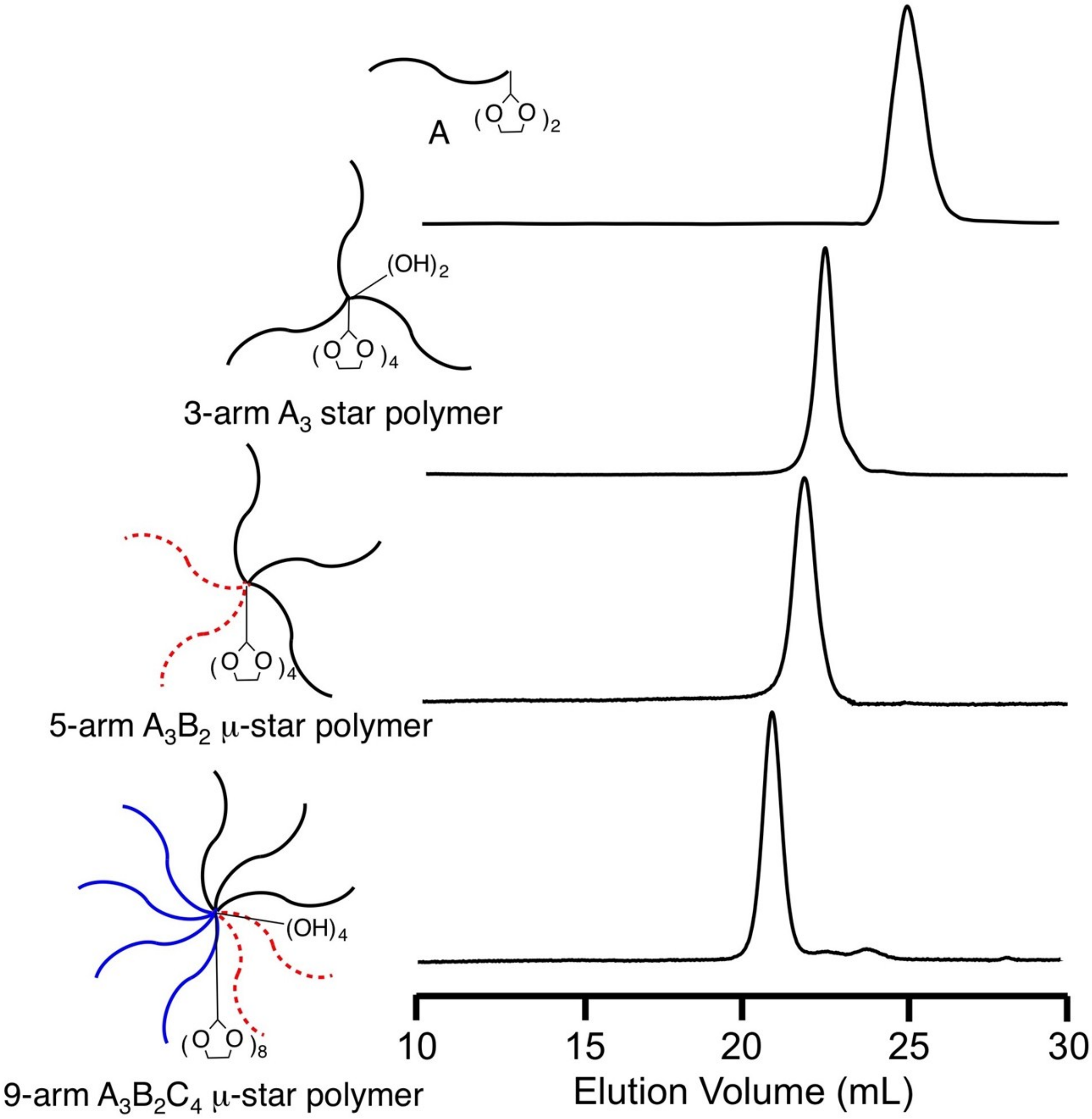
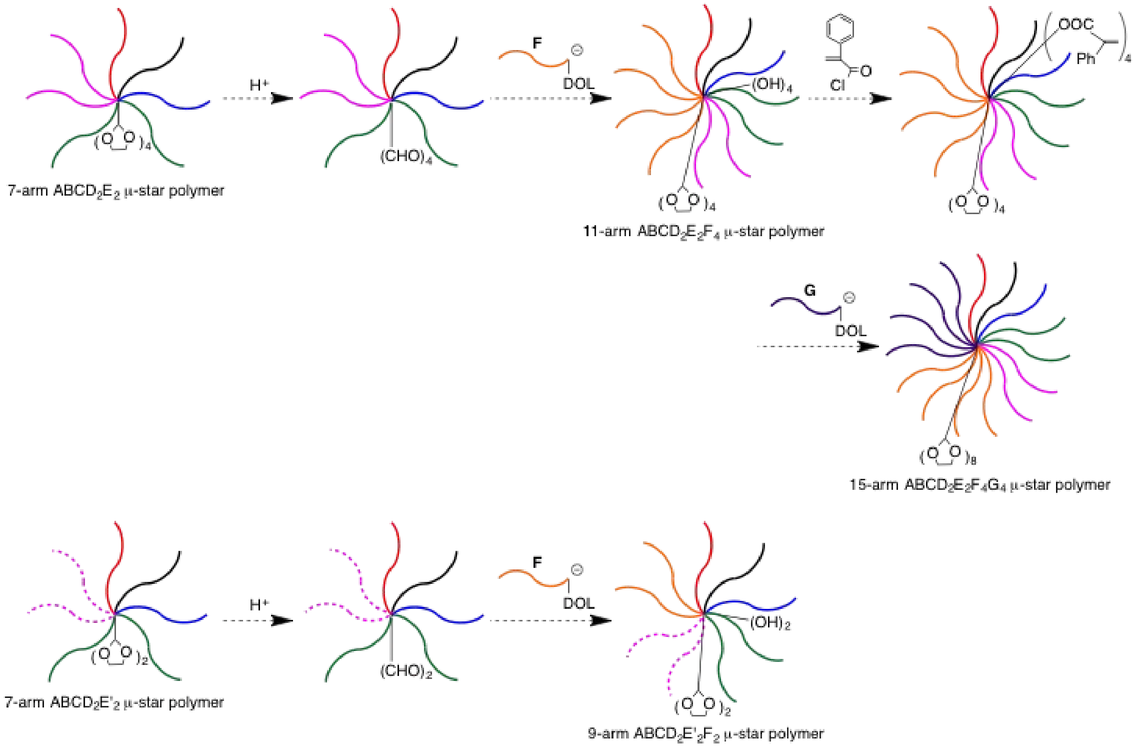


Fig S5. SEC profiles from A, 3-arm A_3, 5-arm A_3B_2, to 9-arm $A_3B_2C_4$ μ-star polymer.



Scheme S1. Synthetic possibility of 11-arm and 15-arm μ-star polymers from 7-arm ABCD$_2$E$_2$ (or E'$_2$) by iterative methodology using chain-end-DOL-functionalized polymer anions.

References

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