

## Supporting Information

# **Syntheses of exactly-defined multi-graft polymers with two or more graft chains per branch point by new iterative methodology**

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## Experimental

### Materials

All chemicals (> 98% purities) were purchased from Sigma Aldrich Japan or Tokyo Chemical Industry Co. Ltd. and used as received unless otherwise stated. Tetrahydrofuran (THF), heptane, styrene, 1,1-diphenylethylene (DPE),  $\alpha$ -methylstyrene ( $\alpha$ MS), 4-methylstyrene (MS), methyl methacrylate (MMA), *tert*-butyl methacrylate (*t*BMA), benzyl methacrylate (BnMA), and (2-methoxyethoxy)ethyl methacrylate (ME2MA) were purified according to the procedures reported elsewhere.<sup>1-</sup>

<sup>3</sup> 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-(3-trimethylsilyloxy-methylphenyl)ethylene (**1**)<sup>1</sup>, 1,4-bis(1-phenylethenyl)benzene (PEB)<sup>4</sup>,  $\alpha$ -phenylacrylic acid (PAA)<sup>5</sup>, 4-*tert*-butyldimethylsilyloxystyrene (SiOS)<sup>6</sup> were synthesized according to the literatures previously reported.

### Measurements

Both <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a Bruker DPX300 in CDCl<sub>3</sub>. Chemical shifts were recorded in ppm downfield relative to CHCl<sub>3</sub> ( $\delta$  = 7.26) and CDCl<sub>3</sub> ( $\delta$  = 77.1) for <sup>1</sup>H and <sup>13</sup>C NMR as standard, respectively. Molecular weights and molecular weight distributions were measured on an Asahi Technieon AT-2002

equipped with a viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1 mL min<sup>-1</sup> at 40 °C. Three columns (Tosoh TSKgel G5000H<sub>HR</sub>, G4000H<sub>HR</sub>, G3000H<sub>HR</sub>) were used. Relative and absolute molecular weights were determined by SEC with refractive index (RI) detection using PS standards, and the combination of viscometer, right angle laser light scattering (RALLS), and RI detection, respectively. Separation of polymer mixture was carried out by preparative SEC (Knauer, smartline) equipped with four columns (Tosoh TSKgel G5000H<sub>HR</sub> x2, G4000H<sub>HR</sub> x2) using THF as a carrier solvent at a flow rate of 5 mL/min at room temperature.

**Synthesis of exactly-defined graft copolymers consisting of a PMMA main chain, and two PS graft chains per branch point.**

The titled compounds were synthesized in similar manners as shown in Scheme 6 except for the use of living PS end-capped with 1,1-diphenylethylene (DPE) instead of living PME2MA. The linking reaction using a living PS end-capped with DPE (1.5 eq. to the PA group) was conducted in THF at -78 °C for 12 h, followed by isolation of the objective polymer by preparative SEC. Characterization results are as follows : **G<sub>2</sub>(x,y)**: x and y are the number of polymer segments corresponding to the PMMA main chain

and PS graft chains, respectively. **G<sub>2</sub>(1,1)** 2.05 g, 92%.  $M_n$  SEC-RALLS = 27.1 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.03 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.23-6.20 (m, Ar), 5.87 (s, CH<sub>2</sub>=), 5.12 (s, Ph-CH<sub>2</sub>O-PA), 4.60 (s, Ph-CH<sub>2</sub>O-Si), 3.60 (s, COOCH<sub>3</sub>), 2.32-0.31 (m, main chain, <sup>s</sup>Bu), 0.03 (s, Si(CH<sub>3</sub>)<sub>2</sub>). **G<sub>2</sub>(1,2)** 1.54 g, 84%.  $M_n$  SEC-RALLS = 36.9 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.05 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.24-6.22 (m, Ar), 5.87 (s, CH<sub>2</sub>=), 5.13 (s, Ph-CH<sub>2</sub>O-PA), 4.60 (s, Ph-CH<sub>2</sub>O-Si), 3.60 (s, COOCH<sub>3</sub>), 2.34-0.31 (m, main chain, <sup>s</sup>Bu). **G<sub>2</sub>(2,3)** 1.36 g, 65%.  $M_n$  SEC-RALLS = 48.7 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.04 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.23-6.21 (m, Ar), 5.87 (s, CH<sub>2</sub>=), 5.12 (s, Ph-CH<sub>2</sub>O-PA), 4.60 (s, Ph-CH<sub>2</sub>O-Si), 3.60 (s, COOCH<sub>3</sub>), 2.31-0.29 (m, main chain, <sup>s</sup>Bu), 0.03 (s, Si(CH<sub>3</sub>)<sub>2</sub>). **G<sub>2</sub>(2,4)** 1.09 g, 72%.  $M_n$  SEC-RALLS = 54.8 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.05 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.25-6.21 (m, Ar), 5.88 (s, CH<sub>2</sub>=), 5.13 (s, Ph-CH<sub>2</sub>O-PA), 4.60 (s, Ph-CH<sub>2</sub>O-Si), 3.61 (s, COOCH<sub>3</sub>), 2.35-0.30 (m, main chain, <sup>s</sup>Bu). **G<sub>2</sub>(3,5)** 0.77 g, 59%.  $M_n$  SEC-RALLS = 64.8 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.06 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.25-6.18 (m, Ar), 5.87 (s, CH<sub>2</sub>=), 5.13 (s, Ph-CH<sub>2</sub>O-PA), 4.60 (s, Ph-CH<sub>2</sub>O-Si), 3.60 (s, COOCH<sub>3</sub>), 2.32-0.28 (m, main chain, <sup>s</sup>Bu), 0.03 (s, Si(CH<sub>3</sub>)<sub>2</sub>). **G<sub>2</sub>(3,6)** 0.05 g, 6%.  $M_n$  SEC-RALLS = 73.0 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.04 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.24-6.20 (m, Ar), 5.87 (s, CH<sub>2</sub>=), 5.13 (s, Ph-CH<sub>2</sub>O-PA), 4.60 (s, Ph-CH<sub>2</sub>O-Si), 3.61 (s, COOCH<sub>3</sub>), 2.35-0.28 (m, main chain, <sup>s</sup>Bu). **G<sub>2</sub>(4,6)** 0.04 g, 75%.  $M_n$  SEC-RALLS = 77.9 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.05 <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.25-6.21 (m, Ar), 4.61 (s, Ph-

$CH_2O-Si$ ), 3.61 (s,  $COOCH_3$ ), 2.36-0.27 (m, main chain,  $^sBu$ ).

### **Synthesis of PMMA-*eg*-PS possessing 3 PA groups at each branch point.**

An in-chain-(PA and TBS ether)-functionalized PS-*b*-PMMA ( $M_n$  SEC-RALLS = 11.6 kg mol<sup>-1</sup>), similarly synthesized as already mentioned, reacted with 3 eq. of a living in-chain-(TMS and TBS ether)-functionalized PS-*b*-PMMA ( $M_n$  calcd = 11.3 kg mol<sup>-1</sup>) in THF at -40 °C for 16 h. The objective graft copolymer **G<sub>3</sub>(2,2)** was isolated by preparative SEC. The TMS ether was transformed into a PA group in similar manners as already mentioned (0.58 g, total 45%).  $M_n$  SEC-RALLS = 22.6 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.02. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.24-6.20 (m, Ar), 5.87 (s,  $CH_2=$ ), 5.12 (s, Ph- $CH_2O$ -PA), 4.60 (s, Ph- $CH_2O$ -Si), 3.60 (s,  $COOCH_3$ ), 2.33-0.31 (m, main chain,  $^sBu$ ), 0.03 (s, Si( $CH_3$ )<sub>2</sub>).

Three eq. of a living in-chain-(TMS and TBS ether)-functionalized PS-*b*-PMMA ( $M_n$  calcd = 11.4 kg mol<sup>-1</sup>) again reacted with the obtained **G<sub>3</sub>(2,2)** to introduce another graft unit. After the isolation by preparative SEC, the TMS ether of the **G<sub>3</sub>(3,3)** was again converted to a PA group (0.28 g, total 56%).  $M_n$  SEC-RALLS = 33.5 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.25-6.19 (m, Ar), 5.87 (s,  $CH_2=$ ), 5.12 (s, Ph- $CH_2O$ -PA), 4.61 (s, Ph- $CH_2O$ -Si), 3.60 (s,  $COOCH_3$ ), 2.37-0.31 (m, main chain,  $^sBu$ ), 0.03 (s, Si( $CH_3$ )<sub>2</sub>).

Finally, 3 eq. of a living PMMA ( $M_n$  calcd = 4.42 kg mol<sup>-1</sup>) reacted with **G<sub>3</sub>(3,3)** in

THF at -40 °C for 16 h to introduce a PMMA segment into the main chain. The objective graft copolymer **G<sub>3</sub>(4,3)** was isolated by precipitation into MeOH twice. Three TBS ethers at each junction was then transformed into three PA groups in similar manners as already mentioned (0.24 g, total 75%).  $M_n$  SEC-RALLS = 36.7 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.25-6.20 (m, Ar), 5.87 (s, CH<sub>2</sub>=), 5.12 (s, Ph-CH<sub>2</sub>O-PA), 4.61 (s, Ph-CH<sub>2</sub>O-Si), 3.60 (s, COOCH<sub>3</sub>), 2.36-0.30 (m, main chain, <sup>s</sup>Bu).

#### **Synthesis of an graft quarterpolymer consisting of PS, PMMA, PMS and P'BMA (G<sub>4</sub>(4,3,3,3)).**

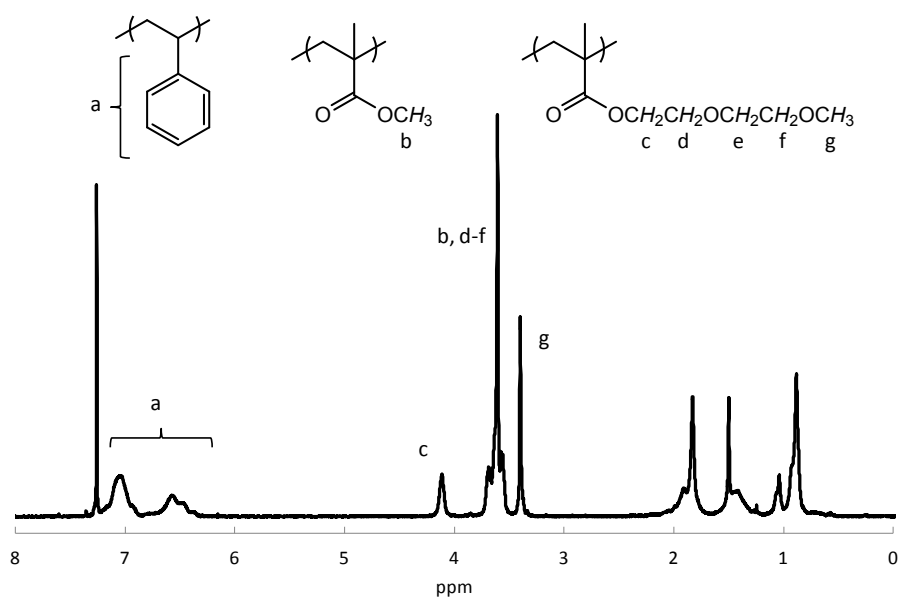
An in-chain-DPE-functionalized PMS-*b*-P'BMA was prepared by sequential anionic polymerization of 4-methylstyrene (8.36 mmol), PEB (0.262 mmol), *tert*-butyl methacrylate (7.13 mmol) initiated with *sec*-BuLi (0.196 mmol) in THF at -78 °C. The block copolymer was purified by precipitation into MeOH three times and freeze-drying from its absolute benzene solution. Oligo( $\alpha$ -methylstyryl)lithium was prepared from *sec*-BuLi (0.0186 mmol) and  $\alpha$ -methylstyrene (0.0621 mmol) and reacted with the in-chain-DPE-functionalized PMS-*b*-P'BMA (0.0191 mmol) in THF at -78 °C for 3 h. Thus prepared block copolymer in-chain anion (3 eq. to the PA group) in situ reacted with **G<sub>3</sub>(4,3)** (0.00208 mmol) under the same conditions for 12 h. The objective graft

quarterpolymer was isolated by preparative SEC (0.09 g, 64%).  $M_n$  SEC-RALLS = 64.8 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.03. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.21-6.13 (m, Ar), 3.61 (s, COOCH<sub>3</sub>), 2.27 (s, Ph-CH<sub>3</sub>), 2.13-0.46 (m, main chain), 1.44 (s, COO'Bu).

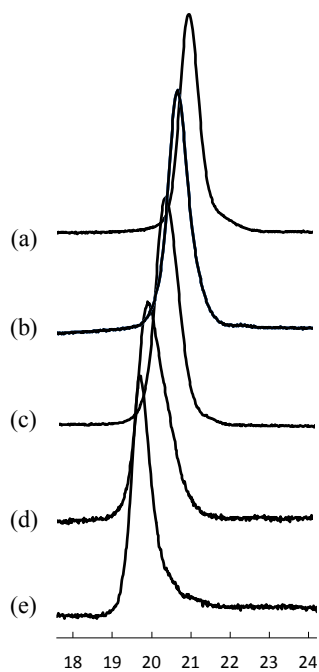
### **Synthesis of an graft quintopolymer consisting of PS, PMMA, PMS, P'BMA, and PSiOS (G<sub>5</sub>(4,3,3,3,3)).**

A living PSiOS end-capped with 3 units of α-methylstyrene (0.0215 mmol,  $M_n$  calcd = 5.02 kg mol<sup>-1</sup>) reacted with in-chain-DPE-functionalized PMS-*b*-P'BMA (0.0212 mmol) in THF at -78 °C for 16 h. Thus prepared 3-arm star polymer in-chain anion in situ reacted with the G<sub>3</sub>(4,3) (different batch,  $M_n$  SEC-RALLS = 48.8 kg mol<sup>-1</sup>, 0.00207 mmol) at the same conditions for 24 h. The objective graft quintopolymer was isolated by preparative SEC (0.10 g, 53%).  $M_n$  SEC-RALLS = 92.0 kg mol<sup>-1</sup>,  $M_w/M_n$  = 1.05. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ = 7.23-6.07 (m, Ar), 3.61 (s, COOCH<sub>3</sub>), 2.28 (s, PhCH<sub>3</sub>), 2.16-0.55 (m, main chain), 1.44 (s, COO'Bu), 0.86 (s, Si'Bu), 0.14 (s, Si(CH<sub>3</sub>)<sub>2</sub>).

## Figures

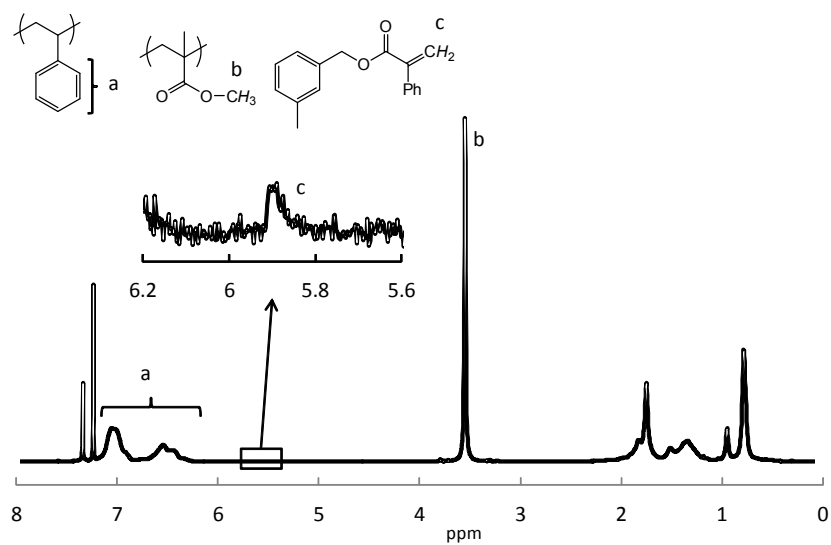


**Fig. S1**  $^1\text{H}$  NMR spectrum of  $\text{G}_1(4,3,3)$ .

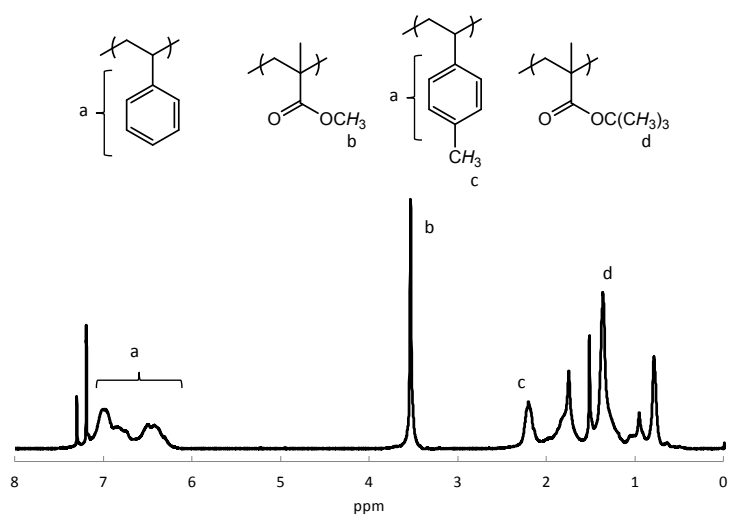


**Fig. S2** SEC curves of a series of  $\text{G}_2$ : (a)  $\text{G}_2(1,1)$ , (b)  $\text{G}_2(1,2)$ , (c)  $\text{G}_2(2,3)$ , (d)  $\text{G}_2(3,5)$ , and (e)  $\text{G}_2(4,6)$ .





**Fig. S3**  $^1\text{H}$  NMR spectrum of PA-functionalized  $\text{G}_3(4,3)$ .



**Fig. S4**  $^1\text{H}$  NMR spectrum of  $\text{G}_4(4,3,3,3)$ .

## References

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