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Facile Synthetic Approach to Exact Graft (Co)polymers and Double-Tailed Polystyrene: Linking Reaction of Living Anionic Polymers with Specially Designed In-Chain-Multifunctionalized Polystyrenes

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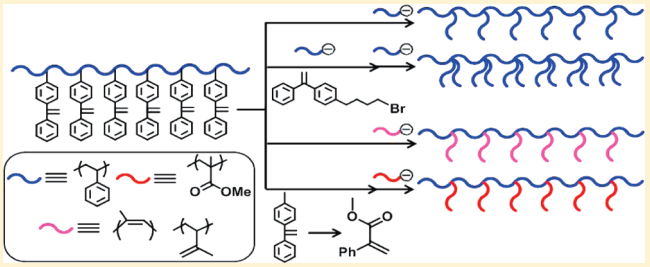
ABSTRACT: This paper describes the facile synthesis of a diverse range of exact graft (co)polymers and double-tailed polystyrene (PS) by a linking reaction of living anionic polymers with a specially designed in-chain-multifunctionalized backbone PS. The backbone PS, precisely controlled in DPE placement and number as well as molecular weight, was prepared by combining the iterative synthetic sequence with the subsequent coupling reaction and then reacted with either of living anionic PS, polyisoprene (PI), or poly(methyl methacrylate) (PMMA). As a result, new exact graft (co)polymers having six PS, six PI, and six PMMA graft chains were successfully synthesized. Furthermore, a new double-tailed exact graft PS having 12 PS graft chains (two PS chains per one branch point) could also be synthesized by repeating twice the addition reaction of living anionic PS to the backbone PS. In the graft (co)polymers herein synthesized, all of the parameters that define the structure of a graft (co)polymer, i.e., molecular weights of the backbone and the graft chains, distance between the graft chains, and the number of branch points, are perfectly controlled.



INTRODUCTION

Graft (co)polymers have been widely studied for a long time because they offer unique and interesting properties, behavior, and morphologies in solution as well as in bulk.[1−18] However, such characteristics have not been well elucidated in regard to their branched structures due to the synthetic difficulties of well-defined graft (co)polymers even at the present time.[19−25] The structure of a graft (co)polymer can be defined by the following three parameters: (1) molecular weight of the backbone chain, (2) molecular weight of the graft chain, and (3) distance (or molecular weight) between the graft chains. An ideal graft (co)polymer, in which all of the above parameters are perfectly controlled, was termed an "exact graft (co)polymer" by Hadjichristidis.[26] Although a variety of graft (co)polymers have been usually synthesized by three general methods, i.e., (a) "grafting from", (b) "grafting onto", and (c) "grafting through" methods, most of graft (co)polymers synthesized are not completely controlled in structure with respect to the three parameters.[1−3,27,28] To the best of our knowledge, only four examples of exact graft (co)polymer have been so far synthesized.[26,29−31]

In 2000, Hadjichristidis and Paraskeva reported the first successful synthesis of an exact graft copolymer composed of a polyisoprene (PI) backbone chain and two polystyrene (PS) graft chains by a stepwise iterative methodology, as illustrated in Scheme 1.[26] The first step was the addition reaction of poly(isoprenyl)lithium (PILi) to 1,4-bis(phenylethenyl)benzene (**1**) to introduce a 1,1-diphenylethylene (DPE) moiety at the chain end. In the second step, the resulting ω-terminal DPE-functionalized PI was reacted with a stoichiometric amount of poly(styryl)lithium (PSLi) to link PS to the PI chain. The thus-prepared AB diblock copolymer with a DPE-derived anion served *in situ* as the macroinitiator in the anionic polymerization of isoprene to prepare a living 3-arm AA′B star-branched polymer in the third step. By repeating the same three reaction steps, an exact graft copolymer having two PS graft chains was synthesized. As can be seen in the resulting graft copolymer, the above three parameters are completely controlled by the molecular

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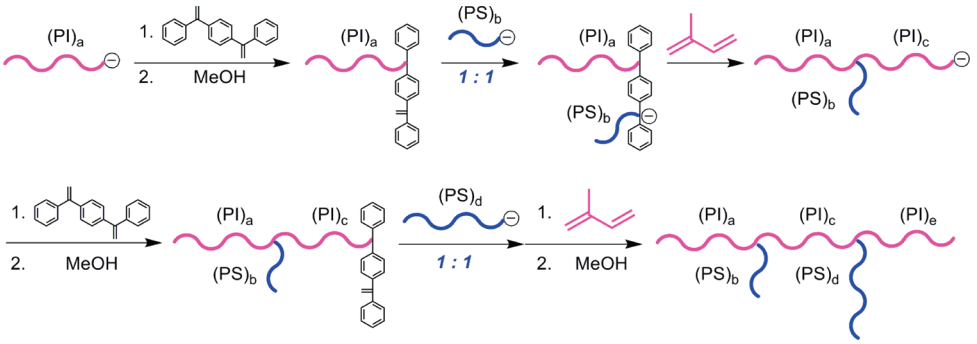
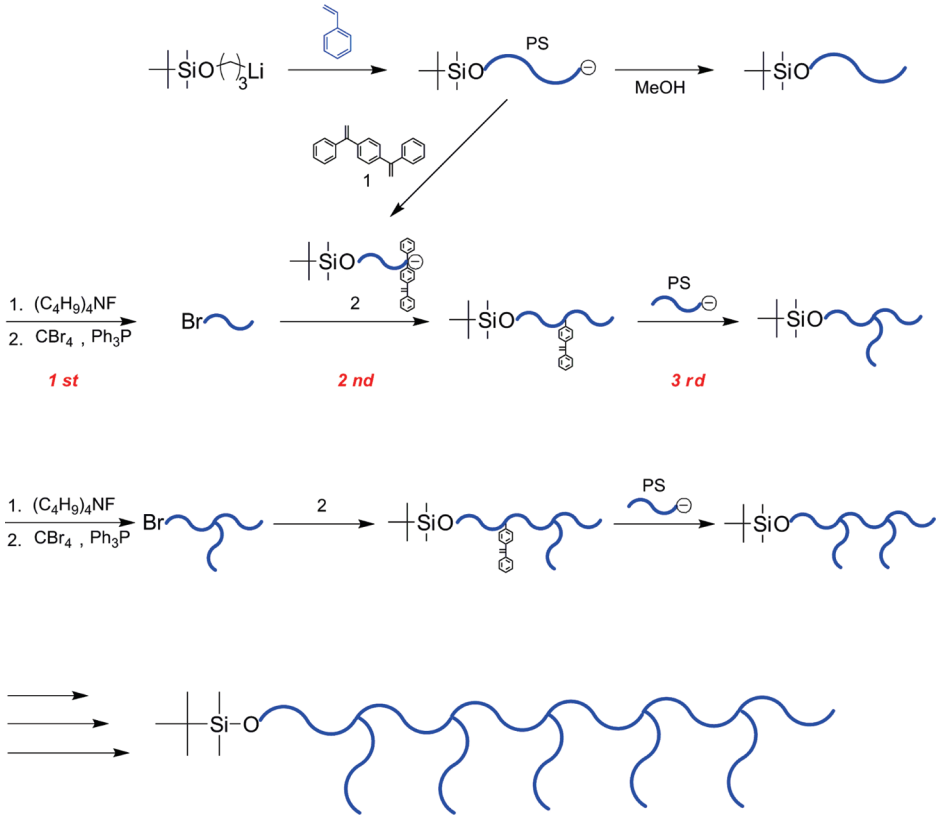
Scheme 1. Synthesis of Exact Graft Copolymer[26]



Scheme 2. Synthesis of Exact Graft PSs Having up to Five Graft Chains[30]



weight of the living polymer of either isoprene or styrene, prepared in each of all reaction steps.

This methodology can offer the potential for providing a general procedure, with which exact graft copolymers with more graft chains can be synthesized by repeating the same reaction steps. However, the synthesis may be limited because a perfect 1:1 stoichiometry, operationally difficult in experiment, is always required in each addition reaction of PSLi to the DPE function introduced at the chain end. Very recently, Hadjichristidis and co-workers synthesized new exact graft poly(1,3-butadiene)s (PBs) (or exact comb PBs) having three PB graft chains by linking intermediate polymers produced by the same methodology.[29]

We have recently proposed a new stepwise iterative methodology, as illustrated in Scheme 2, in order to establish a more convenient and general methodology for the synthesis of exact graft (co)polymers having more graft chains.[30] In this methodology, premade living anionic polymers are used as the building blocks and connected to each other via linking reactions to build up exact graft polymers.

In the first step, an α-(3-bromopropyl)-functionalized PS was prepared by the living anionic polymerization of styrene with 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium (SiOPLi), followed by transformation of the α-terminal SiOP group into a 3-bromopropyl function by treatment first with $(C_4H_9)_4NF$ (deprotection) and then with CBr_4 and Ph_3P (bromination). In the second step, an α-SiOP-*ω*-DPE-functionalized living PS, **2**, was prepared by the polymerization of styrene with SiOPLi in the same manner and subsequently by end-capping with **1**. The resulting **2** reacted *in situ* with the α-(3-bromopropyl)-functionalized PS prepared in the first step to link the two PS chains,

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resulting in an α-SiOP-in-chain-DPE-functionalized $(PS)_2$. In the third step, a newly prepared PSLi reacted with the DPE function in the PS chain to introduce a PS graft chain. Thus, one graft unit with the α-terminal SiOP group (convertible to the 3-bromopropyl function) was prepared.

Since the three reaction steps were observed to be virtually quantitative, the same sequence, including the three reaction steps, was repeated four more times to synthesize a series of exact comb PSs having up to five PS graft chains, in which the above-mentioned four parameters are perfectly controlled by the molecular weight of the living PS prepared in each step. More importantly, the addition reaction step shown in Scheme 1,[26] which requires an exact 1:1 stoichiometry between the reagents, could be avoided in this methodology. This makes it possible to continue the iterative synthetic sequence more times, resulting in the synthesis of exact graft polymers with more graft chains. Although the developed methodology is thus effective for the synthesis of exact graft (co)polymers, the synthesis requires laborious multistep reactions. For example, at least 10 linking reaction steps were needed to synthesize an exact comb PS having five PS graft chains. Therefore, the next synthetic aim is to reduce the number of reaction steps and to establish a more convenient and general synthetic procedure for exact graft (co)polymers.

Herein, we report on a further successful development of the previous methodology effective for the synthesis of exact graft (co)polymers, with which a diverse range of exact (co)polymers including a double-tailed exact graft PS are synthesized by fewer numbers of reaction steps.

EXPERIMENTAL SECTION

Materials. The reagents (>98% purities) were purchased from Aldrich Japan and used as received unless otherwise stated. Styrene, 1,1-diphenylethylene (DPE), isoprene, methyl methacrylate (MMA), THF, heptane, *tert*-butylbenzene, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), CH_2Cl_2, CBr_4, and LiCl were purified by usual manners. Bu_2Mg, BuLi, *sec*-BuLi, and 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium purchased from FMC Corp., Lithium Division, were diluted with heptane in appropriate concentrations under high-vacuum conditions and used. Styrene was finally distilled from its Bu_2Mg (ca. 3 mol %) solution on the vacuum line. Isoprene and DPE were finally distilled from their ca. 3 mol % BuLi solutions on the vacuum line. MMA was finally distilled from its $(C_8H_{17})_3Al$ solution on the vacuum line. Ph_3P, diisopropyl azodicarboxylate (DIAD), and $(C_4H_9)_4NF$ in THF solution (1 M) were purchased from Tokyo Kasei Kogyo Co., Ltd., Japan, and used as received. 1,4-Bis(phenylethenyl)benzene (**1**) and 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene (**4**) were synthesized according to the procedures previously reported.[32,33] α-Phenyacrylic acid was synthesized by the procedure previously reported.[34]

Measurements. Both ^1H and ^{13}C NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $CHCl_3$ (δ 7.26) and $CDCl_3$ (δ 77.1) for ^1H and ^{13}C NMR as standard, respectively. Molecular weights and polydispersity indices were measured on an Asahi Techneion AT-2002 equipped with a Viscotek TDA model 302 triple detector array using THF as a carrier solvent at a flow rate of 1.0 mL/min at 30 °C. Three PS gel column (pore size (bead size)) were used: 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm). The relative molecular weights were determined by SEC with RI detection using standard polystyrene or poly(methyl methacrylate) calibration curve. The combination of viscometer, right angle laser light scattering detection (RALLS), and RI detection was applied for the online SEC system in order to determine the absolute molecular weights of homopolymers, in-chain-functionalized polymers, and exact graft (co)polymers.

Synthesis of Exact Comb PS, Exact Graft Copolymers, and Double-Tailed Exact Graft PS. Except for deprotection and transformation reactions, all of the polymerizations and linking reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors equipped with break-seals. The reactors were sealed off from the vacuum line and prewashed with a red 1,1-diphenylhexyllithium (ca. 0.05 M) in heptane solution prior to the polymerizations and reactions. All operations were performed according to the usual high-vacuum technique with break-seals.

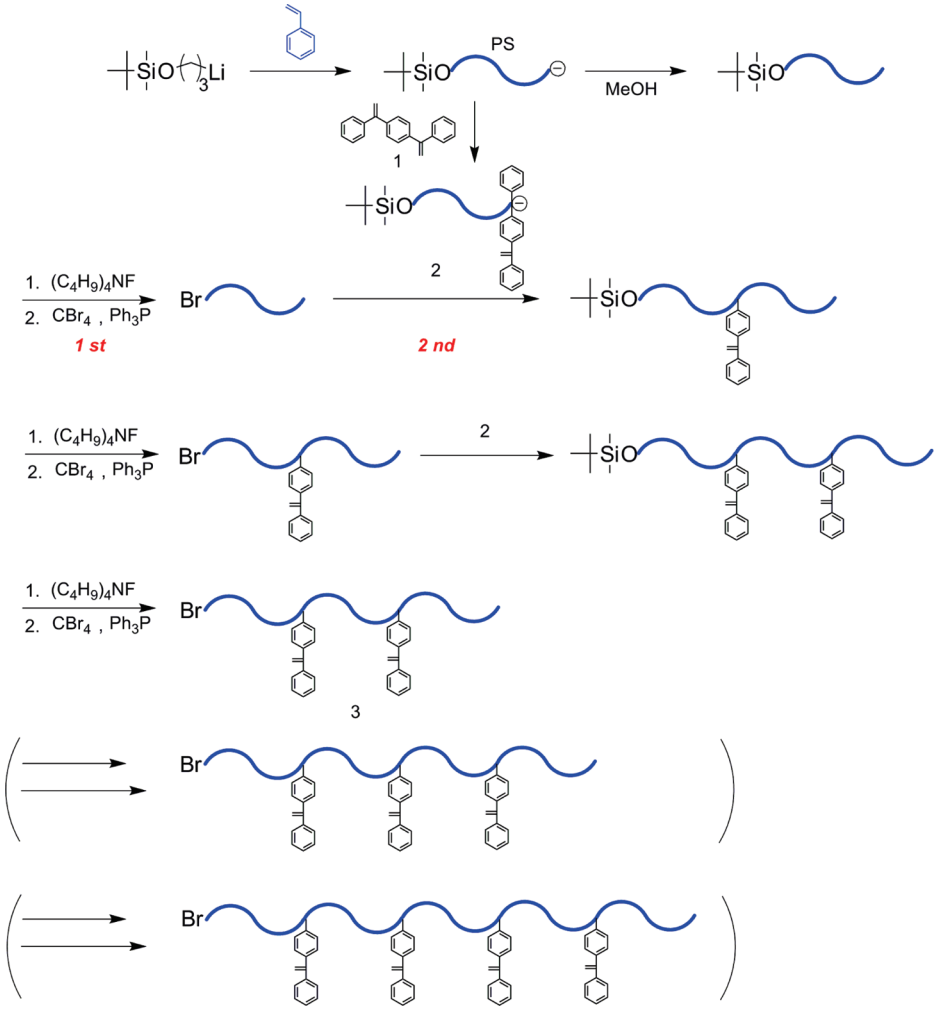
Preparation of α-(3-Bromopropyl)-In-Chain-$(DPE)_2$-Functionalized $(PS)_3$. An α-SiOP-in-chain-DPE-functionalized $(PS)_2$ (6.46 g) was prepared by the same procedure as that reported previously.[30] ^1H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 5.40 (m, CH_2=C), 3.46 (s, Si−O−CH_2−), 2.3−1.2 (m, −CH_2−CH−), 0.86 (s, −C(CH_3)$_3$), 0.01 (s, Si(CH_3)$_2$). M_n (SEC-RALLS) = 19 300 g/mol, M_w/M_n = 1.03.

The α-SiOP-in-chain-DPE-functionalized $(PS)_2$ (5.80 g, 0.301 mmol for the α-terminal SiOP group) dissolved in dry THF (50 mL) was treated with $(C_4H_9)_4NF$ (15.0 mmol) in dry THF solution (15.0 mL) at 25 °C for 12 h under a nitrogen atmosphere. After quenching the reaction with methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The resulting polymer was purified by reprecipitation twice from THF to methanol (5.48 g, 94% yield). Complete deprotection was confirmed by the disappearance of signals for Si−CH_3 and C−CH_3 protons at 0.01 and 0.86 ppm, respectively. ^1H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 5.40 (m, CH_2=C), 3.48 (s, −O−CH_2−), 2.3−1.2 (m, −CH_2−CH−). M_n (SEC-RALLS) = 19 000 g/mol, M_w/M_n = 1.03.

The resulting polymer (5.38 g, 0.283 mmol for 3-hydroxypropyl group) dissolved in dry THF (45 mL) was reacted with CBr_4 (3.92 mmol) and Ph_3P (7.70 mmol) in dry THF (20 mL) at 0 °C for 0.5 h and then at 25 °C for 12 h under a nitrogen atmosphere. The reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer thus obtained was purified by reprecipitation twice from THF to methanol (5.18 g, 96% yield). The degree of bromination was quantitative by comparing the ^1H NMR signal area of Br−CH_2 protons at 3.23 ppm with that of PS and DPE phenyl protons at 6.4−7.2 ppm. The quantitative bromination was also confirmed by the observation that the signal for CH_2 protons was completely shifted from 3.48 to 3.23 ppm. More importantly, the signal at 5.40 ppm for CH_2=C protons of the DPE function was observed to remain unchanged, clearly exhibiting that the DPE function remained as such under the bromination conditions. ^1H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 5.40 (m, CH_2=C), 3.23 (s, Br−CH_2−), 2.3−1.2 (m, −CH_2−CH−).

The objective α-SiOP-in-chain-$(DPE)_2$-functionalized $(PS)_3$ was prepared as follows: Styrene (42.4 mmol) in *tert*-butylbenzene solution (19.9 mL) was polymerized with SiOPLi (0.446 mmol) in the presence of TMEDA (1.29 mmol) in heptane solution (3.63 mL) in the same manner as that mentioned above. The living PS solution thus prepared was cooled to −78 °C, and THF (25.0 mL) precooled at −78 °C was added. Then, **1** (0.782 mmol) in THF solution (12.6 mL) was added to the living PS solution at −78 °C, and the reaction mixture was allowed to stand at −78 °C for 2 h. The resulting α-SiOP-ω-DPE-functionalized living PS reacted *in situ* with the α-(3-bromopropyl)-in-chain-DPE-functionalized $(PS)_2$ (4.82 g, 0.254 mmol for 3-bromopropyl group) dissolved in THF (20.5 mL) at −78 °C for 5 min and then for 25 °C for 12 h. The polymers were precipitated in methanol. The linked polymer was isolated in 82% yield (5.94 g) by fractional precipitation using a mixture of cyclohexane and hexane. The ^1H NMR signals at 5.40, 0.86, and 0.01 ppm corresponding to CH_2=C protons of the two DPE functions and C−CH_3 and Si−CH_3 protons of the initiator residue were

Scheme 3. Preparation of α-(3-Bromopropyl)-In-Chain-$(DPE)_2$-Functionalized $(PS)_3$



clearly observed at reasonable signal areas. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 5.40 (m, CH_2=C), 3.46 (s, Si−O−CH_2−), 2.3−1.2 (m, −CH_2−CH−), 0.86 (s, −C(CH_3)$_3$), 0.01 (s, Si(CH_3)$_2$). M_n (SEC-RALLS) = 28 500 g/mol, M_w/M_n = 1.03.

Under an atmosphere of nitrogen, the resulting polymer (5.80 g, 0.201 mmol for SiOP group) dissolved in dry THF (50 mL) was deprotected by treatment with $(C_4H_9)_4NF$ (7.40 mmol) in dry THF solution (7.40 mL). After quenching the reaction with methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was purified by precipitation twice from THF to methanol. Thus, an α-(3-hydroxypropyl)-in-chain-$(DPE)_2$-functionalized $(PS)_3$ was obtained in 88% yield (5.10 g). Then, the resulting polymer (4.96 g, 0.173 mmol for 3-hydroxypropyl group) dissolved in THF (40 mL) was reacted with CBr_4 (2.24 mmol) and Ph_3P (3.98 mmol). The same work-up gave an α-(3-bromopropyl)-in-chain-$(DPE)_2$-functionalized $(PS)_3$ in 94% yield (4.66 g). The degree of bromination was confirmed to be quantitative by comparing the ^{1}H NMR signal area of Br−CH_2 protons at 3.23 ppm with that of PS and DPE phenyl protons at 6.4−7.2 ppm. The quantitative bromination was also confirmed by the observation that the signal for CH_2 protons was completely shifted from 3.48 to 3.23 ppm. Again importantly, the signal at 5.40 ppm for CH_2=C protons of the DPE function remained unchanged under the bromination conditions. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 5.40 (m, CH_2=C), 3.23 (s, Br−CH_2−), 2.3−1.2 (m, −CH_2−CH−). M_n (SEC-RALLS) = 28 800 g/mol, M_w/M_n = 1.03.

Preparation of In-Chain-$(DPE)_6$-Functionalized $(PS)_7$. The title polymer was prepared by the coupling reaction between the α-(3-bromopropyl)-in-chain-$(DPE)_2$-functionalized $(PS)_3$ and a newly prepared α,ω-$(DPE)_2$-functionalized difunctional living PS. Styrene (6.08 mmol) in THF solution (6.20 mL) was polymerized with lithium naphthalenide (0.134 mmol) in THF solution (4.04 mL) at −78 °C for 0.5 h. Then, **1** (0.186 mmol) in THF solution (6.02 mL) was added to the living PS solution in THF at −78 °C for 1 h. The resulting α,ω-$(DPE)_2$-functionalized difunctional living PS (0.134 mmol) reacted *in situ* with the α-(3-bromopropyl)-in-chain-$(DPE)_2$-functionalized $(PS)_3$ (4.62 g, 0.160 mmol for 3-bromopropyl group) dissolved in THF (36.2 mL) at −78 °C for 1 h and then at 25 °C for 12 h. After quenching the reaction with degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymers. The target linked polymer was isolated in 70% yield first by fractional precipitation using a mixture of cyclohexane and hexane. Since the isolated polymer still included both higher and lower molecular weight fractions (∼8% and ∼6%), they were completely removed by SEC fractionation prior to the next polymer synthesis in each case. The ^{1}H NMR signal at 5.40 ppm for the DPE CH_2=C protons was clearly observed at a reasonable signal area corresponding to six DPE functions incorporated in the PS chain. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4

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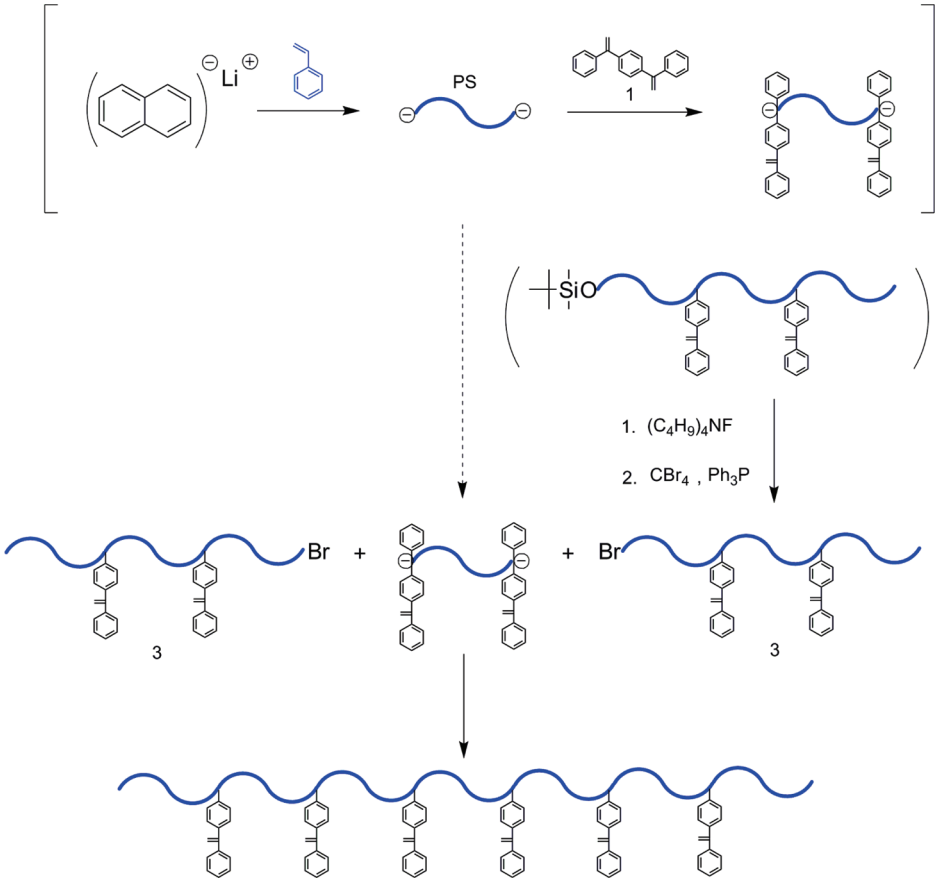
Scheme 4. Synthesis of In-Chain-$(DPE)_6$-Functionalized $(PS)_7$



(m, aromatic), 5.40 (m, CH_2═C), 2.3−1.2 (m, −CH_2−CH−). M_n (SEC-RALLS) = 65.9 kg/mol, M_w/M_n = 1.04.

Synthesis of Exact Comb PS. The title comb PS was synthesized by the reaction of PSLi with the backbone PS. Styrene (11.1 mmol) in THF solution (12.0 mL) was polymerized with *sec*-BuLi (0.106 mmol) in heptane solution (1.98 mL) at −78 °C for 0.5 h and *in situ* added to the in-chain-$(DPE)_6$-functionalized $(PS)_7$ (M_n = 65.9 kg/mol, 0.505 g, 0.0460 mmol for six DPE functions (0.00766 mmol × 6)) dissolved in THF (5.50 mL) at −78 °C, and the reaction mixture was allowed to react at −78 °C for 12 h. Then, the reaction mixture was reacted with **4** (0.142 mmol) in THF solution (2.02 mL) at −78 °C for 8 h to reintroduce the DPE functions via the DPE-derived anions generated at the linking points. After quenching the reaction with degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymers. The linked polymer was isolated in 78% yield (0.750 g) first by fractional precipitation using a mixture of cyclohexane and hexane and then by SEC fractionation. It was purified by precipitation twice and freeze-dried from its absolute benzene solution. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 5.40 (m, CH_2═C), 2.3−1.2 (m, −CH_2−CH−). M_n (SEC-RALLS) = 126 kg/mol, M_w/M_n = 1.03.

Synthesis of Double-Tailed Exact Graft PS. The title polymer was synthesized by the reaction of PSLi with the exact comb PS in-chain-functionalized with six DPE functions synthesized as above. Styrene (6.05 mmol) in THF solution (6.25 mL) was polymerized with *sec*-BuLi (0.0680 mmol) in heptane solution (1.25 mL) at −78 °C for 0.5 h and reacted *in situ* with the exact comb PS (M_n = 126 kg/mol, 0.625 g, 0.0298 mmol for six DPE functions) dissolved in THF (3.75 mL) at −78 °C for 12 h. After quenching the reaction with degassed methanol, the reaction mixture was precipitated into a large amount of methanol to precipitate the polymers. The target polymer was isolated in 86% yield (0.785 g) by fractional precipitation using a mixture of cyclohexane and hexane and then by SEC fractionation and freeze-dried. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 2.3−1.2 (m, −CH_2−CH−). M_n (SEC-RALLS) = 184 kg/mol, M_w/M_n = 1.05.

Synthesis of PS-*exact graft*-PI. The title exact graft copolymer was synthesized by the addition reaction of PILi, end-capped with a few styrene units, to the backbone PS. Isoprene (11.0 mmol) in heptane solution (2.95 mL) was polymerized with *sec*-BuLi (0.122 mmol) in heptane solution (2.30 mL) at 30 °C for 0.5 h and at 40 °C for an additional 2 h. The PILi solution was cooled to −78 °C, and THF (25.0 mL) precooled at −78 °C was added to the solution. Then, styrene (1.04 mmol) in THF solution (1.07 mL) was added to end-cap the chain-end. The resulting PILi end-capped with a few styrene units (M_n = 7350 g/mol, 0.122 mmol) reacted *in situ* with in-chain-$(DPE)_6$-functionalized $(PS)_7$ (M_n = 65.9 kg/mol, 0.445 g, 0.0405 mmol for six DPE functions) dissolved in THF (4.49 mL) at −78 °C for 12 h. After quenching the reaction with degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymers. The target exact graft copolymer was isolated in 62% yield (0.515 g) by fractional precipitation using a mixture of hexane and 2-propanol and then by SEC fractionation. The polymer was purified by reprecipitation twice and freeze-dried from its absolute benzene solution. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 5.1−5.0 (m, −CH═CH−), 4.8−4.7 (m, −CH═CH_2−), 2.3−1.2 (m, −CH_2−CH−), 1.6 (m, −CH_2═C(CH_3)−). M_n (SEC-RALLS) = 117 kg/mol, M_w/M_n = 1.02.

Synthesis of PS-*exact graft*-PMMA. The title polymer was synthesized by the addition reaction of living PMMA to the in-chain-(α-phenyl acrylate (PA))$_6$-functionalized $(PS)_7$. A new backbone

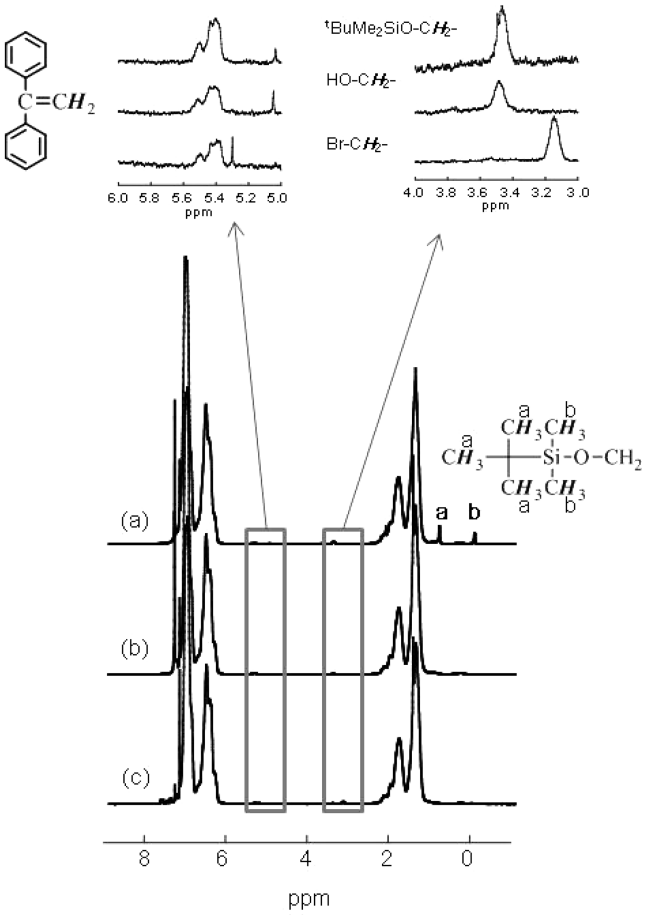


Figure 1. ^{1}H NMR spectra of in-chain-DPE-functionalized PS α-terminal-functionalized with (a) 3-(*tert*-butyldimethylsilyloxy)propyl group, (b) 3-hydroxypropyl group, and (c) 3-bromopropyl group.

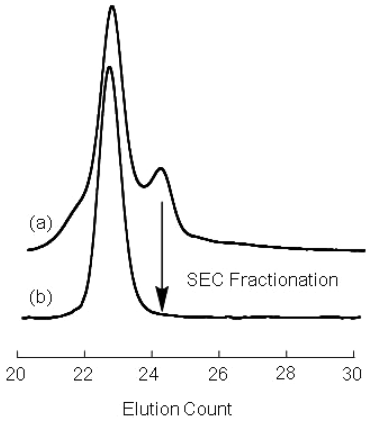


Figure 2. Preparation of in-chain-$(DPE)_6$-functionalized $(PS)_7$ before (a) and after SEC fractionation (b).

polymer having more reactive six PA functions, the in-chain-$(PA)_6$-functionalized $(PS)_7$, was prepared as follows: The in-chain-$(DPE)_6$-functionalized $(PS)_7$ (M_n = 65.9 kg/mol, 0.381 g, 0.0347 mmol for six DPE functions) dissolved in *tert*-butylbenzene (14.0 mL) was reacted with SiOPLi (0.282 mmol) in the presence of TMEDA (0.864 mmol) at 0 °C for 0.5 h and at 30 °C for 4 h. After quenching the reaction with degassed methanol, the polymer was precipitated in methanol, purified by reprecipitation twice from the THF solution to methanol, and freeze-dried from its absolute benzene solution for 20 h (0.321 g, 84% yield). The degree of functionalization was determined to be virtually quantitative by comparing the ^{1}H NMR signal area of Si−CH_3 protons at 0.01 ppm with that of PS and DPE phenyl protons at 6.4−7.2 ppm. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 3.46 (s, Si−O−CH_2−), 2.3−1.2 (m, −CH_2−CH−), 0.86 (s, −$C(CH_3)_3$), 0.01 (s, $Si(CH_3)_2$).

Table 1. Synthesis of In-Chain-$(DPE)_6$-Functionalized $(PS)_7$

	$M_n \times 10^{-3}$ (g/mol)			M_w/M_n
polymer	calcd.	SEC[a]	RALLS[b]	SEC[a]
PS-D6[c]	66.9	65.9	65.9	1.04

[a] Estimated by SEC with standard polystyrenes. [b] Determined by SEC equipped with triple detectors. [c] In-chain-$(DPE)_6$-functionalized $(PS)_7$.

Under a nitrogen atmosphere, the resulting polymer (0.268 g, 0.0244 mmol for six SiOP groups) dissolved in dry THF (5.0 mL) was treated with $(C_4H_9)_4NF$ (0.500 mmol) in dry THF solution (5.0 mL) at 25 °C for 12 h. After quenching the reaction with methanol, the polymer was precipitated in methanol. The resulting polymer was reprecipitated twice from THF to methanol (0.208 g, 78%). ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 3.48 (s, HO−CH_2−), 2.3−1.2 (m, −CH_2−CH−).

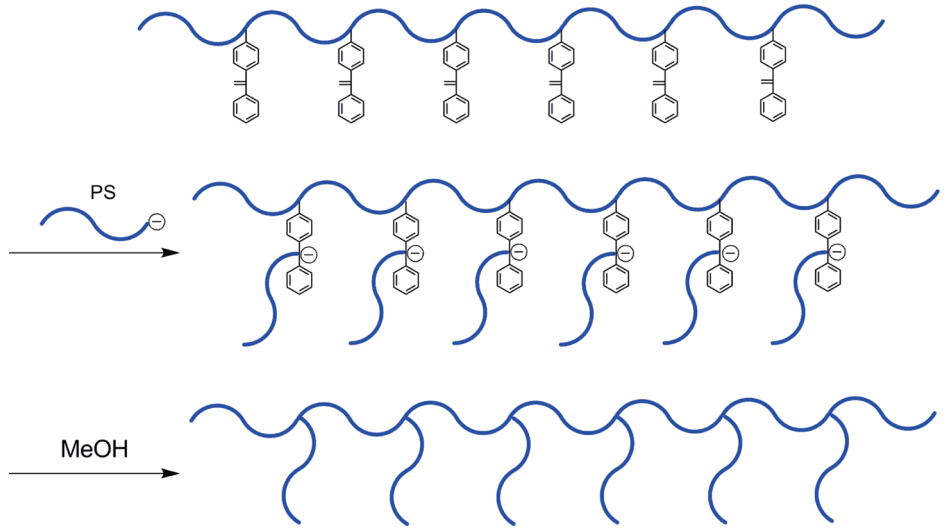
Under a nitrogen atmosphere, the resulting polymer (0.202 g, 0.0183 mmol for six OH groups) dissolved in dry THF (5.0 mL) was mixed with α-phenylacrylic acid (1.08 mmol) and PPh_3 (1.07 mmol), followed by the subsequent addition of DIAD (1.08 mmol) dissolved in dry THF (5.0 mL) to the reaction mixture at 0 °C. The mixture was allowed to react at 30 °C for 24 h. After quenching the reaction with methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. It was purified by reprecipitation twice from THF to methanol. Thus, the target in-chain-$(PA)_6$-functionalized $(PS)_7$ (0.133 g, 66%) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.2−6.2 (m, aromatic), 5.86 (s, C=CH_2), 5.06 (s, Ph−CH_2−O−C(=O)), 2.3−1.2 (m, −CH_2−CH−).

MMA (10.0 mmol) in THF solution (7.19 mL) was polymerized at −78 °C for 0.5 h with the initiator prepared from *sec*-BuLi (0.0922 mmol) and DPE (0.144 mmol) in THF (6.00 mL) in the presence of LiCl (0.412 mmol). The resulting living PMMA was mixed with the in-chain-$(PA)_6$-functionalized $(PS)_7$ (0.132 g, 0.0120 mmol for six PA groups) dissolved in THF (2.00 mL) at −78 °C, and the reaction mixture was allowed to react at −40 °C for 24 h. After quenching the reaction with degassed methanol, the resulting polymers were precipitated in methanol, followed by fractional precipitation, a pure PS-*exact graft*-PMMA (0.142 g, 56%) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.2−6.4 (m, aromatic), 4.65 (s, −CH_2−O−), 3.60 (s, −OCH_3), 2.3−1.2 (m, −CH_2−CH− and −CH_2−$C(CH_3)$−), 1.1−0.5 (m, −CH_2−$C(CH_3)$−). M_n (SEC-RALLS) = 128 kg/mol, M_w/M_n = 1.03.

RESULTS AND DISCUSSION

Preparation of In-Chain-$(DPE)_6$-Functionalized $(PS)_7$ Used as a Backbone Polymer. In the methodology previously reported by us, the premade functional living polymer is always linked to another polymer chain or graft polymer unit in each reaction step to build up a series of exact graft polymer.[30] Therefore, the structure of the synthesized graft polymer can be precisely controlled and intentionally changed to any desired structure. However, laborious multistep reactions are required throughout the synthesis. In practice, at least 10 linking reaction steps were used in the total synthesis of an exact comb PS having five PS graft chains as mentioned in the Introduction.

Scheme 5. Synthesis of Exact Graft Comb PS



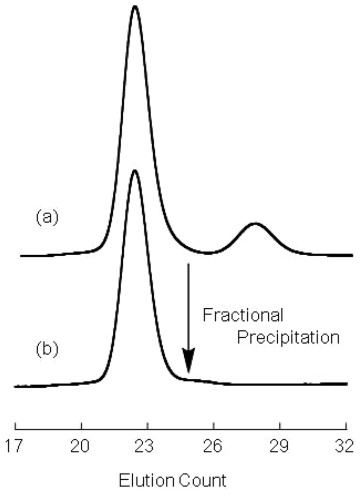


Figure 3. SEC profiles of the reaction mixture (a) and exact graft comb PS having six PS graft chains obtained by fractional precipitation (b).

In order to reduce the number of reaction steps and to establish a more convenient and general methodology, we have herein designed to first prepare an in-chain-DPE-multifunctionalized PS, precisely controlled in DPE placement and number as well as molecular weight, as the backbone chain and then to react it with living anionic polymers to introduce the corresponding graft chains. Schemes 3 and 4 show the synthetic outline of the backbone chain by combining the iterative synthetic sequence involving two reaction steps with the subsequent coupling reaction. The two reaction steps are as follows: (1) a transformation reaction of the SiOP α-terminus introduced in the polymer into a 3-bromopropyl function used as the next reaction site and (2) a coupling reaction of the resulting α-(3-bromopropyl)-functionalized PS with the α,ω-functionalized living PS, **2**, to link the two PS chains.

Similar to the preparation shown in Scheme 2, the α-SiOP-in-chain-DPE-functionalized $(PS)_2$ was prepared by reaction steps 1 and 2. All of the reactions were monitored by ^{1}H NMR, SEC, and SEC-RALLS to be virtually quantitative.

The resulting α-SiOP-in-chain-DPE-functionalized $(PS)_2$ was treated with $(C_4H_9)_4NF$ (deprotection) and then with CBr_4 and Ph_3P (bromination) to transform the SiOP α-terminus into the 3-bromopropyl function. These reactions were observed by ^{1}H NMR to be 100%, as shown in Figure 1. The most important point in this transformation reaction is that the bromination reaction takes place quantitatively, while the DPE function incorporated into the PS chain remains completely intact under such conditions (see also Figure 1). The second step involved a coupling reaction between the resulting α-(3-bromopropyl)-in-chain-DPE-functionalized $(PS)_2$ and a 1.7-fold excess of a newly prepared **2**. The SEC profile of the reaction mixture exhibited two peaks: a higher molecular weight one for the linked product and the other one for the deactivated **2** used in excess in the reaction. In addition, the formation of a small amount of high-molecular-weight shoulder (ca. 5%) was observed. This may be formed by the undesirable Li−Br exchange reaction, followed by the reactions among the intermediate polymers. The α-SiOP-in-chain-$(DPE)_2$-functionalized $(PS)_3$ was isolated by fractional precipitation using a mixed solvent of cyclohexane and hexane. The high-molecular-weight fraction observed as the shoulder was removed by using SEC fractionation, since the complete removal was difficult by fractional precipitation. The isolated polymer was again brominated by the same treatment as that described, resulting in an α-(3-bromopropyl)-in-chain-$(DPE)_2$-functionalized $(PS)_3$, **3**. It was also confirmed by the ^{1}H NMR analysis that two DPE functions remained as such and the bromination was quantitative.

It may be possible to continue the same reaction sequence to prepare a backbone PS having three or more DPE functions (see also Scheme 3). However, we have carried out the coupling reaction of 2 equiv of the resulting brominated PS with difunctional living PS, as shown in Scheme 4, to extend the backbone chain length from $(PS)_3$ to $(PS)_7$ and to increase the number of DPE functions from two to six only by one step. For this coupling reaction, a new difunctional living PS α, ω-functionalized with DPE moieties was prepared by the living anionic polymerization of styrene with lithium naphthalenide, followed by end-capping with **1**, and subsequently

Table 2. Synthesis of Exact Comb PS and Exact Graft Copolymers

	$M_n \times 10^{-3}$ (g/mol)			M_w/M_n	composition (PS/PI or PS/PMMA, w/w)	
polymer	calcd.	SEC[a]	RALLS[b]	SEC[a]	calcd	obsd
PS-D6[c]	66.9	65.9	65.9	1.04		
PS-$(PS)_6$[d]	128	87.6	126	1.03		
PS-$(PI)_6$[e]	111	86.0	117	1.02	60/40	56/43
PS-$(PMMA)_6$[f]	132	101	128	1.03	51/50	51/50

[a] Estimated by SEC with standard polystyrenes. [b] Determined by SEC equipped with triple detectors. [c] In-chain-$(DPE)_6$-functionalized $(PS)_7$ used as a backbone polymer. [d] Exact comb PS having six PS graft chains. [e] PS-*exact graft*-PI having six PI graft chains. [f] PS-*exact graft*-PMMA having six PMMA graft chains.

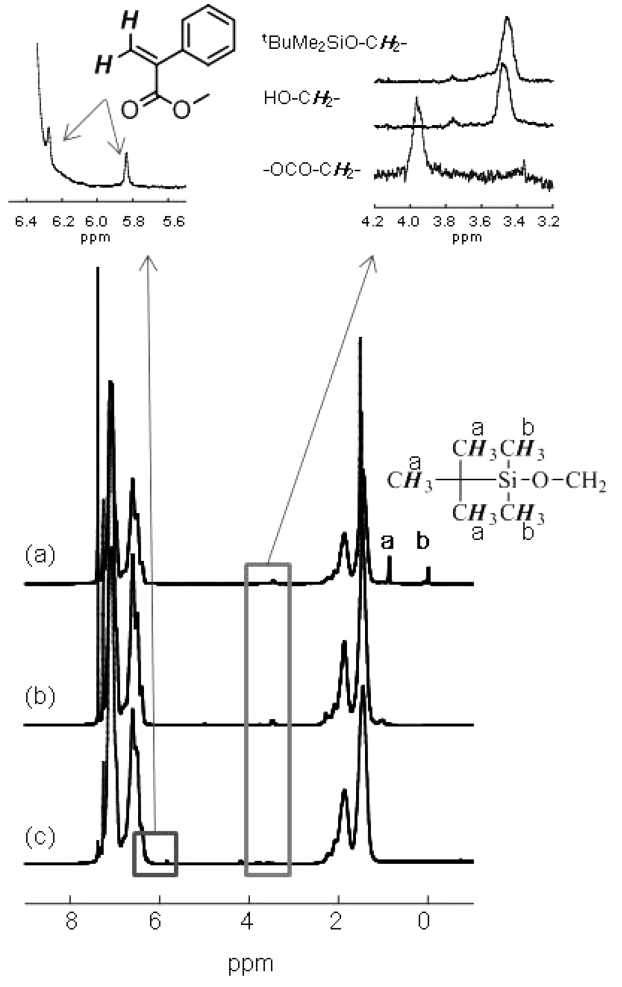


Figure 4. ^{1}H NMR spectra of PS in-chain-multifunctionalized with (a) 3-*tert*-butyldimethylsilyloxy group, (b) hydroxyl group, and (c) α-phenyl acrylate group.

coupled *in situ* with the brominated PS, **3**, in THF at −78 °C for 1 h and at 25 °C for an additional 12 h.

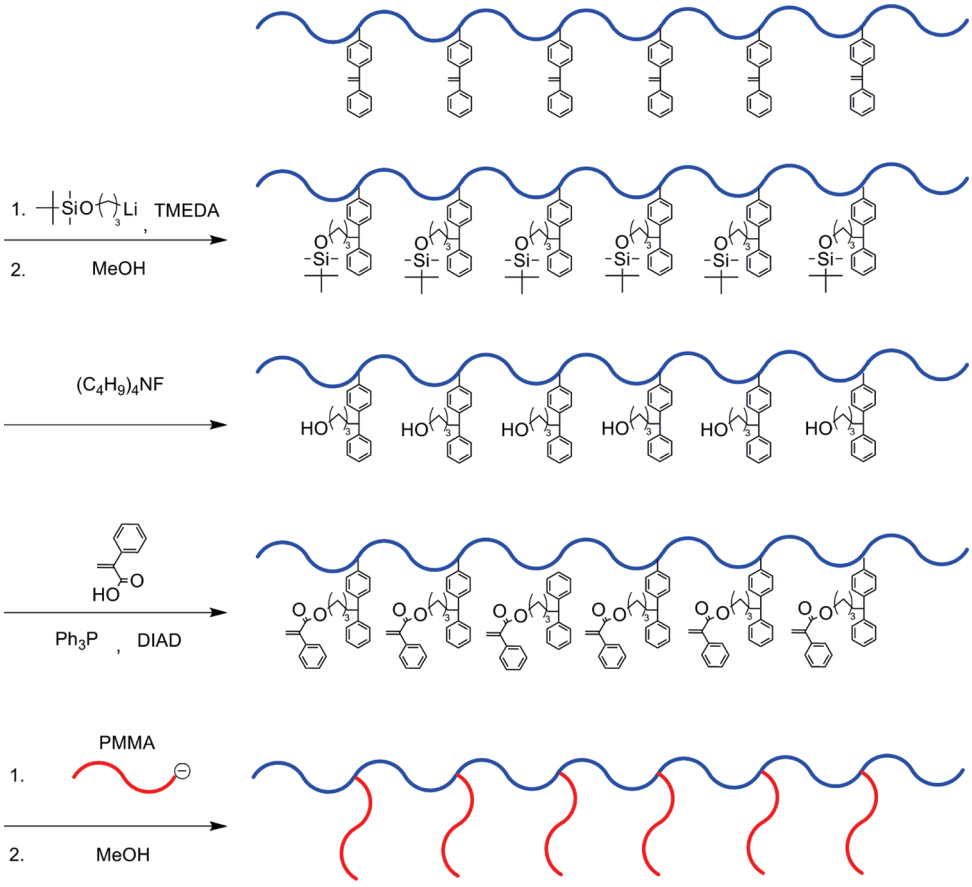
The SEC profile of the reaction mixture, as shown in Figure 2a, exhibited three peaks for the target coupled product and small amounts of a high-molecular-weight shoulder (ca. 8%) and a low-molecular-weight tail (ca. 20%). The high-molecular-weight shoulder may be formed by the Li−Br exchange reaction, followed by coupling reactions among the intermediate polymers, while the latter low-molecular-weight tail is considered to be the unreacted **3** used in excess in the reaction. In addition, an α-DPE-in-chain-$(DPE)_3$-functionalized $(PS)_4$, which was the 1:1 adduct between **3** and the difunctional living PS, might also be included. Overall, the reaction efficiency was estimated to be around 85%. It should be mentioned that the occurrence of the Li−Br exchange reaction was negligible in the first reaction step between **2** (M_n = 10 200 g/mol) and the α-(3-bromopropyl)-functionalized PS (M_n = 8900 g/mol). However, similar exchange reactions, followed by coupling reactions among the intermediate polymers, appeared to occur to greater extents in the second (∼5%) and the final coupling reactions (∼8%) among the higher-molecular-weight polymers, although they were not significant (<10%).

The target in-chain-$(DPE)_6$-functionalized $(PS)_7$ was roughly isolated in 70% yield by fractional precipitation using a mixture of cyclohexane and hexane. Since the isolated polymer still includes the higher-molecular-weight fraction (shoulder) (∼8%) and a small amount of the lower-molecular-weight fraction (tail) (∼6%), both fractions were completely removed by SEC fractionation prior to each graft (co)polymer synthesis. The isolated polymer possessed a sharp monomodal distribution and a predictable molecular weight, as shown in Table 1 and Figure 2b. The molecular weight corresponds to the total molecular weight of all living PSs. Each of the DPE placements can be precisely controlled by the molecular weight of each PSLi. Thus, the target DPE-multifunctionalized PS used as the backbone polymer has been successfully synthesized. In this synthesis, the number of reaction steps has been greatly reduced by employing the coupling reaction at the final stage. If the same backbone polymer would be prepared in a stepwise fashion, at least six coupling reactions are needed. On the other hand, the target polymer could be actually prepared by only three coupling reactions, as shown in Scheme 4.

Synthesis of Exact Comb PS and Exact Graft Copolymers. As illustrated in Scheme 5, an exact comb PS having six PS graft chains was synthesized by the addition reaction of PSLi to the backbone PS. At first, PSLi (M_n = 10 200 g/mol) was prepared by the polymerization of styrene with *sec*-BuLi and reacted *in situ* with the backbone PS (M_n = 65 900 g/mol) in THF at −78 °C. A 2.2-fold excess of PSLi toward the DPE reaction site was used. After 12 h, the reaction was quenched with degassed methanol and the polymers were precipitated in methanol.

The SEC profile shows only two peaks corresponding to the target linked polymer and the deactivated PSLi used in excess in the reaction (Figure 3a). No intermediate peak between the two peaks was present, indicating that the addition reaction cleanly and quantitatively proceeded. It should be mentioned that higher-molecular-weight fractions, often produced by the Wurtz-type

Scheme 6. Synthesis of In-Chain-$(PA)_6$-Functionalized $(PS)_7$ and PS-*exact graft*-PMMA Having Six PMMA Graft Chains



coupling reaction between the brominated PS and living PS, were not formed in this addition reaction. The reaction efficiency was estimated to be nearly quantitative by comparing the two peak areas. The target polymer was isolated by fractional precipitation and finally purified by SEC fractionation. As shown in Figure 3b, the final isolated polymer possessed a sharp monomodal SEC distribution. The molecular weight (M_n = 128 kg/mol) determined by SEC-RALLS was in good agreement with that calculated (M_n = 126 kg/mol) (Table 2). These results show that the resulting polymer is the requisite exact comb PS having six PS graft chains.

The synthesis of a PS-*exact graft*-PI having six PI graft chains was attempted in a similar manner by a reaction of PILi with the same backbone PS. PILi was prepared by the polymerization of isoprene with *sec*-BuLi in heptane at 30 °C for 0.5 h and then at 40 °C for 2 h. The resulting PILi solution was cooled to −78 °C, an equal volume of THF precooled to −78 °C was added, and the backbone PS was subsequently added to react with PILi. A 2-fold excess of PILi was used for each DPE reaction site. However, the reaction occurred only to a small extent (<10%) even after 24 h. The reaction efficiency was not improved by taking either a longer reaction time of 48 h or the use of a 4-fold excess of PILi. Thus, PILi was much less reactive than PSLi toward the DPE function in the PS chain.

Since PSLi quantitatively underwent the addition reaction to the DPE reaction sites of the same backbone PS as mentioned above, PILi was end-capped with a few styrene units and then *in situ* reacted with the backbone PS in order to complete the addition reaction. A 3.0-fold excess of PILi was used for each DPE function. After the usual work-up, the polymer was isolated first by fractional precipitation, followed by SEC fractionation. The isolated polymer was observed to possess a sharp monomodal SEC distribution (M_w/M_n = 1.02). The results, as listed in Table 2, show the polymer to have a molecular weight and a composition in agreement with both the calculated values. Thus, the end-capping of PILi with a few styrene units is very effective to facilitate the addition reaction, giving a new well-defined PS-*exact graft*-PI having six PI graft chains.

In contrast to PSLi, the chain-end enolate anion of living PMMA cannot react with the DPE reaction site at all under normal conditions. Therefore, it is necessary to replace the DPE function by a more reactive reaction site. For this purpose, an α-phenyl acrylate (PA) function seems to be appropriate because of the quantitative linking reaction of the PA function with living PMMA, as reported in our previous paper.[35] The transformation reaction leading to PA function was monitored by ^{1}H NMR to be virtually quantitative, as shown in Figure 4. The synthetic outlines for an in-chain-$(PA)_6$-functionalized $(PS)_7$ used as the backbone polymer and a PS-*exact graft*-PMMA are shown in Scheme 6. At first, an 8-fold excess of SiOPLi reacted with the in-chain-$(DPE)_6$-functionalized $(PS)_7$ in *tert*-butylbenzene in the presence of TMEDA at 0 °C for 0.5 h and at 30 °C for 4 h. On mixing SiOPLi with the backbone PS, an immediate color change to a dark red, characteristic of a DPE-derived anion, was observed, indicating a rapid reaction. SEC profiles of the polymers obtained before and after the reaction were exactly the same in shape and

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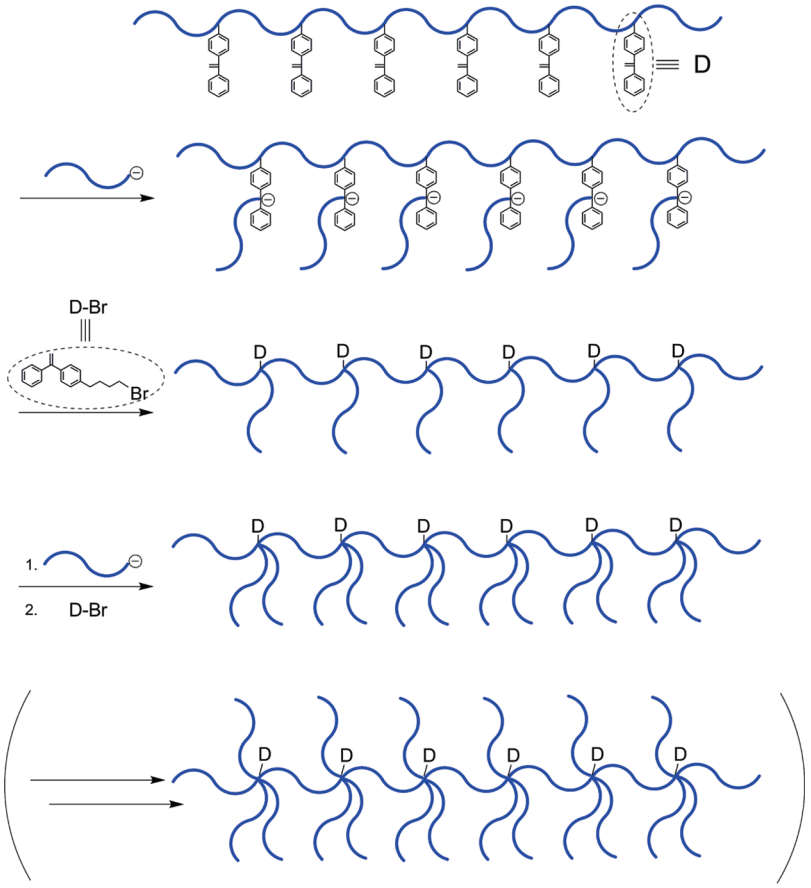
Scheme 7. Synthesis of Double-Tailed Exact Graft PS Having 12 PS Graft Chains (Two PS Chains per One Branch Point)



elution volume. Both characteristic signals at 0.01 and 0.86 ppm, respectively assigned to the silylmethyl and *tert*-butyl protons, were clearly observed in the ^{1}H NMR spectrum of the polymer obtained after the reaction. The reaction yield was estimated to be quantitative based on these peaks. It was also supported by the complete disappearance of the signal at 5.40 ppm corresponding to CH_2═C protons of the DPE function in the same spectrum. The resulting polymer was first treated with $(C_4H_9)_4NF$ (deprotection) and then with α-phenylacrylic acid under the conditions of the Mitsunobu esterification reaction to convert it to PA function. The reactions were monitored by ^{1}H NMR and found to be quantitative within analytical errors.

Living PMMA (M_n = 10 900 g/mol) was prepared by the polymerization of MMA with the initiator from *sec*-BuLi and DPE in the presence of LiCl and *in situ* reacted with the in-chain-$(PA)_6$-functionalized $(PS)_7$ (M_n = 65 900 g/mol) in THF at −78 °C. The reaction mixture was allowed to react at −40 °C for 24 h. The quantitative reaction was confirmed by the SEC profile of the polymer mixture. The linked polymer was isolated by fractional precipitation. The characterization results, also given in Table 2, show that the molecular weight distribution is monomodal and sharp (M_w/M_n = 1.03) and that the M_n value (128 kg/mol) determined by SEC-RALLS agrees very well with that calculated (M_n = 132 kg/mol). The composition observed by ^{1}H NMR is consistent with that calculated from the feed ratio. Each of these data is a strong proof that the requisite PS-*exact graft*-PMMA having six PMMA graft chains has been successfully synthesized. Thus, the PA reaction site works satisfactorily and may possibly be used in the linking reaction with living anionic polymers of other methacrylate monomers.

Synthesis of Double-Tailed Exact Graft PS. The same backbone PS is usable for the synthesis of double-tailed exact graft PS, as illustrated in Scheme 7. By a reaction of PSLi with in-chain-$(DPE)_6$-functionalized $(PS)_7$ (M_n = 65 900 g/mol) and subsequent *in situ* treatment with 1-(4-(4-bromobutyl)phenyl)-1-phenylethylene (**4**), six PS graft chains as well as six DPE reaction sites at the linking points could be introduced into the backbone PS. The two reaction steps were monitored by ^{1}H NMR spectra and SEC and shown to be quantitative in THF at −78 °C for 12 h and at −78 °C for 8 h, respectively. The reaction was terminated with degassed methanol, and the polymers were precipitated in methanol.

The in-chain-$(DPE)_6$-functionalized exact comb PS thus prepared was reacted with a newly prepared PSLi in THF at −78 °C for 24 h. A characteristic dark red color appeared instantaneously on mixing in PSLi, indicating that the addition reaction rapidly occurred. The SEC profile of the reaction mixture exhibited only two peaks for the linked product and the deactivated PSLi used in excess in the reaction. No intermediate peak was present between the two peaks. Moreover, higher-molecular-weight fractions were not formed. The reaction efficiency was estimated to be almost quantitative by comparing the two SEC peak areas. The target polymer was isolated by fractional precipitation and further purified by SEC fractionation. The resulting polymer possesses a sharp monomodal SEC distribution (M_w/M_n = 1.05). The molecular weight (M_n = 184 kg/mol) determined by

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Table 3. Synthesis of Double-Tailed Exact Graft PS

	$M_n \times 10^{-3}$ (g/mol)			M_w/M_n
polymer	calcd	SEC[a]	RALLS[b]	SEC[a]
PS-D6[c]	66.9	65.9	65.9	1.04
PS-$(PS)_6$[d]	128	87.6	126	1.03
PS-$(PS_2)_6$[e]	183	101	184	1.05

[a] Estimated by SEC with standard polystyrenes. [b] Determined by SEC equipped with triple detectors. [c] In-chain-$(DPE)_6$-functionalized $(PS)_7$. [d] An exact comb PS having six PS graft chains. [e] Double-tailed exact graft PS having 12 PS graft chains (two PS chains per one branch point).

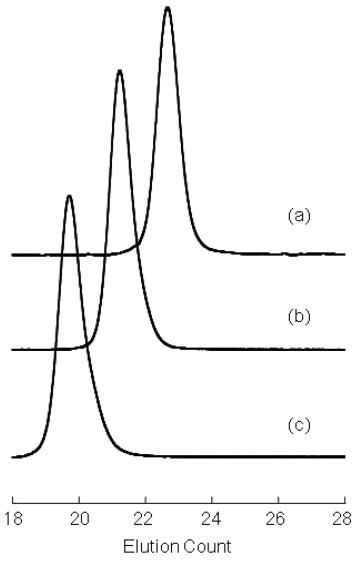

Figure 5. SEC profiles of in-chain-$(DPE)_6$-functionalized $(PS)_7$ (a), exact graft comb PS (b), and double-tailed exact graft PS (c).

SEC-RALLS agreed well with the predicted value (M_n = 183 kg/mol), as summarized in Table 3. Thus, the target double-tailed exact graft PS having 12 PS graft chains (two PS chains per one branch point) was successfully synthesized by repeating the addition reaction of PSLi twice. Figure 5 shows SEC profiles of the backbone PS, the exact comb PS, and the double-tailed exact graft PS for comparison. As the final polymer, prior to quenching, possesses six DPE-derived anions generated by the addition reaction with PSLi, a further introduction of PS graft chains may be possible by repeating the same reaction steps, as also shown in Scheme 7.

CONCLUSIONS

We have herein successfully synthesized a diverse range of new exact graft (co)polymers (PS backbone chain) having six PS, six PI, and six PMMA graft chains as well as a double-tailed exact graft PS with well-defined structures by the addition reaction of living anionic polymers with a specially designed backbone PS in-chain-functionalized with six DPE or PA reaction sites.

As compared with the previous methodology reported by us,[30] there are two advantages in the present methodology. First, the specially designed backbone PS was prepared by combining the iterative synthetic sequence with the subsequent coupling reaction. With use of the coupling reaction, the number of DPE reaction sites increased from two to six and the chain length of the backbone PS was extended from $(PS)_3$ to $(PS)_7$ only by one step. If the same backbone PS would be prepared in a stepwise fashion, four more coupling reactions are required. Moreover, each coupling reaction step always involves the transformation reaction and the isolation step, and therefore, more time-consuming processes must be carried out. Thus, the use of the coupling reaction enables the number of reaction steps to be significantly reduced. Second, a diverse range of exact graft (co)polymers could be synthesized from the same backbone polymer, in-chain-$(DPE)_6$-functionalized $(PS)_7$. Thus, the synthetic possibility of exact graft (co)polymers having many graft chains has been demonstrated by the success of this work. It should be however noted that many graft chains can be simultaneously introduced by one step, but only the same chains in molecular weight and chemical structure can be introduced to the backbone polymer in the present methodology. Unfortunately, one cannot intentionally change the molecular weight and chemical structure of each graft chain to be introduced. In the synthesis, we have always used graft chains having molecular weights of around 10 000 g/mol, as probably higher molecular weight polymers lead to crowding problems and thus less efficient linking reactions. Therefore, the relationship of possible distance between branching points along the main chain and length of graft chains will be the next target for the synthesis of exact graft (co)polymers.

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