7820 *Macromolecules* **2009**, *42*, 7820–7827
DOI: 10.1021/ma9015455

Macromolecules
ARTICLE

Precise Synthesis of Exact Graft Copolymers, Poly(methyl methacrylate)-*exact graft*-polystyrene, by Iterative Methodology Using a Specially Designed In-Chain-Functionalized AB Diblock Copolymer Anion

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Received July 16, 2009; Revised Manuscript Received September 3, 2009

ABSTRACT: The synthesis of a series of exact graft copolymers composed of poly(methyl methacrylate) (PMMA) backbone chains and PS graft chains up to five in number by a new iterative methodology is described. In this methodology, an in-chain-functionalized AB diblock copolymer (PS-*block*-PMMA) anion with 3-(*tert*-butyldimethylsilyloxymethyl)phenyl (SiOMP) group between the PS and PMMA blocks is used as a key building block specially designed to simultaneously introduce both backbone and graft chains. The methodology involves the following three reaction steps in the entire iterative reaction sequence: (1) a living anionic block copolymerization to prepare the above-mentioned in-chain-SiOMP-functionalized AB diblock copolymer anion, (2) a transformation of the SiOMP group to benzyl bromide (BnBr) function, and (3) a coupling reaction of the in-chain-SiOMP-functionalized AB diblock copolymer anion with the in-chain-BnBr-functionalized block copolymer. By repeating the reaction sequence five times, a series of well-defined exact graft copolymers composed of PMMA backbone chains and PS graft chains up to five in number were successively synthesized. In the graft copolymers herein synthesized, not only the molecular weights of the backbone and graft chains but also the distance between the branch points and the number of graft PS chains are perfectly controlled.

Introduction

A graft copolymer is a polymer consisting of two or more numbers of branch (graft) chains connected to the backbone chain. Since the backbone and graft chains are in general thermodynamically incompatible, most graft copolymers are multiphase materials exhibiting unique and interesting morphologies.[1,2] Because of such morphological behaviors, graft copolymers are often used as emulsifiers, coating materials, adhesives, and compatibilizing agents for polymer blends.

The structure of graft copolymer can be defined by the following four parameters: (1) molecular weight of the backbone chain, (2) molecular weight of the graft chain, (3) distance (or molecular weight) between the branch points, and (4) number of the graft chains along the backbone chain. An ideal graft copolymer, in which all of the above parameters are perfectly controlled, is named "*an exact graft copolymer*" by Hadjichristidis.[3] Although several attempts have been made to synthesize the ideal graft copolymers, most of the graft copolymers so far synthesized were not completely controlled in structure with respect to such parameters.[4−6] Until now, only one exact graft copolymer having two graft chains has been synthesized by living anionic polymerization using 1,4-bis(phenylethenyl)benzene (PEB), as illustrated in Scheme 1.[3]

The first step was the addition reaction of poly(isoprenyl)-lithium (PILi) to PEB to introduce a 1,1-diphenylethylene (DPE) moiety at the chain-end. The resulting ω-terminal DPE-functionalized PI was reacted with a stoichiometric amount of poly(styryl)lithium (PSLi) in a 1:1 addition manner to link the two polymer chains with the generation of a DPE-derived anion at the linking point. Isoprene was *in situ* polymerized with this polymer anion to prepare a living 3-arm star-branched copolymer, followed by reacting with PEB to introduce the DPE moiety at the chain-end. By repeating the same reaction sequence, the objective graft copolymer was obtained.

The distances from the chain-end to the first PS graft, between the first and the second PS grafts, and from the second PS graft to the opposite chain-end are individually controlled by the molecular weights of living (PI)s prepared by the three polymerization steps, shown as $(PI)_a$, $(PI)_b$, and $(PI)_c$ in Scheme 1. The backbone and graft chains are constructed by (PILi)s and (PSLi)s and therefore precisely controlled in molecular weight and composition. Thus, all of the four parameters are perfectly controlled in the resulting polymer, and to the best of our knowledge, this is the first successful synthetic example of exact graft copolymer having two graft chains. The methodology can offer the potential for providing a general procedure for exact graft copolymers with more graft chains by repeating the same reaction sequence mentioned above. However, the synthesis remained at the stage of graft copolymer having two graft chains. This is probably because an exact 1:1 stoichiometry, which is practically difficult in experimental operation, is always required in each addition reaction of PSLi to the DPE moiety in the polymer chain. For such a situation, the synthesis of exact graft copolymers having more graft chains is still a challenging subject even at the present time.

Very recently, Hadjichristidis et al. reported the synthesis of exact comb polybutadienes with two and three branches.[7] Two methodologies have been developed based on the combination reactions of a 3-arm living star polybutadiene and a 1,1-diphenylethylene derivative containing dichloro(methyl)silyl group. However, these procedures are not iterative methodology; therefore, it is difficult to increase the number of graft chains.

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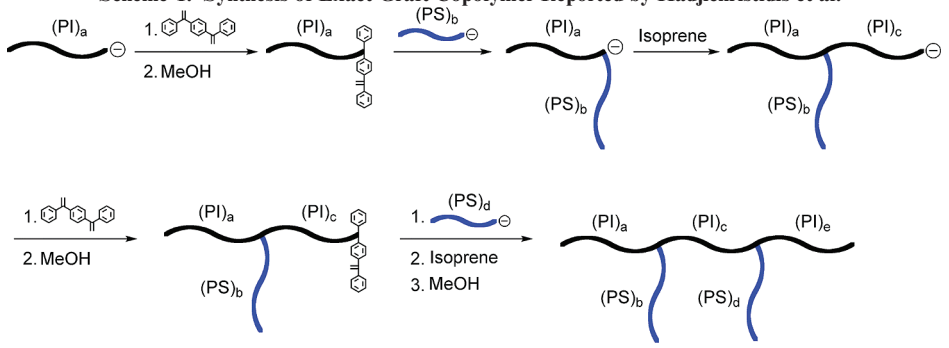
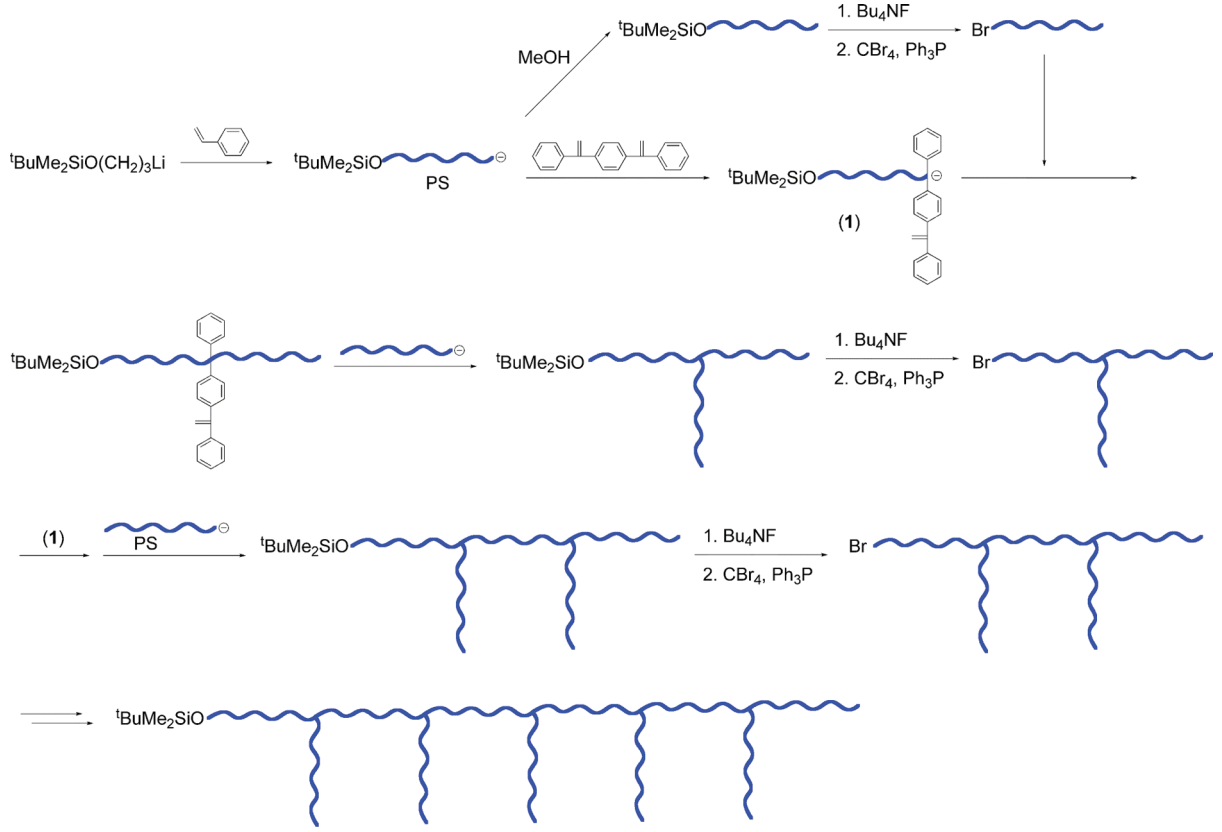
 Published on Web 09/28/2009

Scheme 1. Synthesis of Exact Graft Copolymer Reported by Hadjichristidis et al.[3]



Scheme 2. Synthesis of Exact Comb Polystyrenes[8]



Coincidentally, we have successfully synthesized a series of exact comb (PS)s having up to five PS branches by developing a new iterative methodology as illustrated in Scheme 2.[8] In this methodology, three reaction steps are employed in each iterative reaction sequence, i.e., (1) a transformation reaction of the α-terminal *tert*-butyldimethylsilyloxypropyl (SiOP) group into bromopropyl function via deprotection of the SiOP group followed by bromination, (2) a linking reaction of α-SiOP-*ω*-DPE-functionalized living PS with α-terminal bromopropyl-functionalized PS to prepare an α-SiOP-in-chain-DPE-functionalized PS backbone chain with the introduction of a DPE moiety between the two PS chains, and (3) an addition reaction of PSLi with the DPE moiety to introduce a PS graft chain.

The first stage of the synthesis is the preparation of a 3-arm star-branched PS with a SiOP terminus. The living anionic polymerization of styrene was carried out with 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium (SiOPLi) as an initiator. After quenching with degassed methanol, the α-terminal SiOP group was transformed into 3-bromopropyl function by treatment with $(C_4H_9)_4NF$, followed by reacting with Ph_3P and CBr_4. Next, an α-SiOP-*ω*-DPE-functionalized living PS was prepared by the same living anionic polymerization of styrene with SiOPLi, followed by addition of PEB. Similar to the addition reaction of PEB to PSLi, only one of the two double bonds of PEB reacted with α-terminal SiOP-functionalized PSLi in a 1:1 addition manner.[9,10] The resulting α-SiOP-*ω*-DPE functionalized living PS was *in situ* reacted with the α-terminal 3-bromopropyl-functionalized PS to link the two PS chain, resulting in the formation of α-SiOP- and in-chain-DPE-functionalized PS. In the final step of the reaction sequence, PSLi was reacted with the DPE moiety incorporated in the PS to introduce a PS segment.

Since the reaction step, in which an exact 1:1 stoichiometry is required, was avoided in this methodology, the above-mentioned same reaction sequence could be repeated at least four more times to successively synthesize the well-defined exact comb (PS)s having up to five PS grafts. As can be seen in Scheme 2, all of the four parameters are perfectly controlled in the resulting graft (PS)s. The synthesis of exact graft copolymers by this iterative methodology has not been attempted yet at the present time.

Herein, we report the synthesis of a series of exact graft copolymers composed of poly(methyl methacrylate) (PMMA) backbone chains and PS graft chains by a new conceptual iterative methodology using an in-chain-functionalized AB diblock copolymer anion specially designed to simultaneously introduce both backbone and graft chains.

Experimental Section

Materials. All of the chemicals were purchased from Aldrich, Japan, and used as received, unless otherwise stated. Tetrahydrofuran (THF) was refluxed over sodium wire, distilled over $LiAlH_4$ under nitrogen, and then distilled from its sodium naphthalenide solution under high-vacuum conditions (10^{-6} Torr). Styrene was washed with aqueous 5% NaOH and water, dried over $MgSO_4$, distilled over CaH_2 under reduced pressures, and then finally distilled in the presence of Bu_2Mg under high-vacuum conditions. Methyl methacrylate (MMA) was washed with aqueous 5% NaOH and water, dried over $MgSO_4$, and distilled over CaH_2 under reduced pressures. It was finally distilled from its 3 mol % $(C_2H_5)_3Al$ solution under high-vacuum conditions. Both LiCl and LiBr were dried at 110 °C under the high-vacuum conditions for 48 h and dissolved in absolute THF in the case of LiCl. Chloroform, acetonitrile, and trimethylsilyl chloride were distilled over CaH_2 under a nitrogen atmosphere.

Measurements. Size exclusion chromatography (SEC) was performed 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 weight of polymer ($M_{n,SEC}$) was calculated by RI detection using standard polystyrene calibration. 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 weight of branched polymers ($M_{n,RALLS}$). 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.

Synthesis of 2-(3-Bromophenyl)-1,3-dioxolane. 3-Bromobenzaldehyde (50.2 g, 272 mmol), ethylene glycol (26.3 g, 424 mmol), and *p*-toluenesulfonic acid (0.240 g, 1.26 mmol) were placed in 500 mL two-necked flask equipped with Dean−Stark head, dissolved in toluene (200 mL), and refluxed for 2.5 h. During refluxing, water was removed several times to shift the equilibrium. The reaction was quenched with aqueous $NaHCO_3$. Then, the organic layer was washed with water and dried over $MgSO_4$ in the presence of K_2CO_3 in order to keep alkalescent conditions. After filtration, the organic layer was concentrated, and the residue was distilled over CaH_2 under reduced pressure (bp: 82 °C/2 mmHg) to yield 2-(3-bromophenyl)-1,3-dioxolane (51.1 g, 223 mmol, 82%) as a colorless liquid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.64−7.25 (m, 4H, Ar), 5.79 (s, 1H, O−CH−O), 4.07 (m, 4H, OCH_2CH_2O).

Synthesis of 2-(3-Folmylphenyl)-1-phenylethanol. To a Grignard reagent prepared from 2-(3-bromophenyl)-1,3-dioxolane (24.5 g, 107 mmol) and magnesium (3.94 g, 162 mmol) in THF (140 mL), THF solution (10 mL) of acetophenone (14.8 g, 123 mmol) was added dropwise at 0 °C under nitrogen. The resulting mixture was stirred at 25 °C for 18 h. It was acidified with 2 N HCl at 0 °C, extracted with ether, and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by flash column chromatography (hexanes/ethyl acetate = 6/1−0/1, v/v) yielded 2-(3-folmylphenyl)-1-phenylethanol (30.8 g, 137 mmol, 61%) as colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 9.99 (s, 2H, CHO), 7.97−7.26 (m, 9H, Ar), 2.32 (s, 3H, CH_3).

Synthesis of 1-(3-Formylphenyl)-1-phenylethylene. 2-(3-Folmylphenyl)-1-phenylethanol (30.8 g, 137 mmol) and *p*-toluenesulfonic acid (0.240 g, 1.26 mmol) were placed in 500 mL two-necked flask equipped with Dean−Stark head, dissolved in toluene (150 mL), and refluxed for 1.5 h. During refluxing, water was removed to shift the equilibrium. The reaction was quenched with aqueous $NaHCO_3$. Then, the organic layer was washed with water and dried over $MgSO_4$. After filtration, the organic layer was concentrated under reduced pressure to yield 1-(3-formylphenyl)-1-phenylethylene (27.9 g, 134 mmol, 98%) as colorless oil. It was used without purification. ^1H NMR ($CDCl_3$, 300 MHz): δ = 10.0 (s, 2H, CHO), 7.86−7.25 (m, 9H, Ar), 5.55 (s, 2H, CH_2=).

Synthesis of 1-(3-Hydroxymethylphenyl)-1-phenylethylene. $NaBH_4$ (6.30 g, 167 mmol) was added to ethanol solution (200 mL) of 1-(3-formylphenyl)-1-phenylethylene (22.8 g, 110 mmol) at 0 °C and stirred at 25 °C for 1.5 h. The reaction was quenched with 2 N HCl, and the resulting solution was concentrated by an evaporator. The organic layer was extracted with ether, washed with water, and dried over $MgSO_4$. After filtration, the organic layer was concentrated under reduced pressure to yield 1-(3-hydroxymethylphenyl)-1-phenylethylene (21.5 g, 102 mmol, 93%) as viscous brownish oil. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.39−7.25 (m, 9H, Ar), 5.46 (s, 2H, CH_2=), 4.68 (s, 2H, CH_2O), 1.74 (broad, 1H, OH).

Synthesis of 1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-phenylethylene (1). *tert*-Butyldimethylsilyl chloride (22.9 g, 152 mmol) was slowly added to a DMF solution (150 mL) containing 1-(3-hydroxymethylphenyl)-1-phenylethylene (21.5 g, 102 mmol) and imidazole (20.8 g, 306 mmol) at 0 °C and stirred at 25 °C for 14 h. After quenching with aqueous $NaHCO_3$, the organic layer was extracted with hexanes, washed with water, and dried over $MgSO_4$ in the presence of K_2CO_3 in order to keep alkalescent conditions. Removal of the solvent under reduced pressure followed by flash column chromatography (hexanes/toluene = 2/1, v/v) yielded the title **1** (21.8 g, 67.1 mmol, 66%) as viscous yellowish oil. It was finally purified by drying under high-vacuum conditions followed by colorimetric titration with *sec*-BuLi from colorless to a very faint pink in color to remove impurities that can react with anionic species. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.28−7.21 (m, 9H, Ar), 5.41 (s, 2H, CH_2=), 4.69 (s, 2H, CH_2O), 0.87 (s, 9H, $C(CH_3)_3$), 0.03 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 150.5 (C=), 141.9, 141.8, 128.7, 128.5, 128.1, 127.2, 126.7, 125.9 (Ar), 114.6 (=CH_2), 65.3 (CH_2O), 26.3 ($C(CH_3)_3$), 18.8 ($C(CH_3)_3$), −4.8 ($Si(CH_3)_2$).

Synthesis of In-Chain-Functionalized PS-*block*-PMMA with 3-(*tert*-Butyldimethylsilyloxymethyl)phenyl (SiOMP) Group and Benzyl Bromide (BnBr) Function. All of the polymerization and linking reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors. The reactors were always prewashed with 1,1-diphenylhexyllithium in heptane and used after being sealed off from a vacuum line. Detailed procedures were reported elsewhere.[11]

PSLi was prepared by the polymerization of styrene (20.0 mmol) in THF (20.2 mL) initiated with *sec*-BuLi (0.372 mmol) at −78 °C for 20 min. Then, a THF solution (10.1 mL) of **1** (0.561 mmol) was added to the PSLi solution at −78 °C. After the reaction was allowed to stand for an additional 30 min at −78 °C, LiCl (2.45 mmol) in THF (6.41 mL) was added at −78 °C, followed by addition of a THF solution (15.5 mL) of MMA (20.2 mmol) at −78 °C with vigorous shaking, and the polymerization was allowed to stand for 30 min. After quenching with degassed methanol, the THF solution was poured into a large excess of methanol to precipitate the polymer. The resulting block polymer was reprecipitated twice from THF to methanol and freeze-dried from its absolute benzene solution for 48 h. The block copolymer was obtained in quantitative yield (3.95 g). The resulting in-chain-SiOMP-functionalized block copolymer was characterized by RALLS and ^1H NMR. $M_{n,RALLS}$ = 12 600, M_w/M_n = 1.03. 300 MHz ^1H NMR ($CDCl_3$, ppm): δ = 7.08−6.51 (broad, 289H, Ar), 4.56 (m, 2H,

CH_2O), 3.61 (s, 187H, OCH_3), 1.95−1.73 (broad, 189H, backbone), 0.76 (s, 182H, CCH_3), 0.17 (s, 6H, $Si(CH_3)_2$).

The in-chain-SiOMP-functionalized PS-*block*-PMMA thus prepared (1.50 g, 0.119 mmol for SiOMP terminus) was treated with LiBr (1.06 g, 12.3 mmol) and $(CH_3)_3SiCl$ (1.57 mL, 12.4 mmol) in a mixed solvent of $CHCl_3/CH_3CN$ (30 mL/22.5 mL) at 40 °C for 24 h in order to transform SiOMP group into BnBr function. After quenching with a small amount of methanol and removing the solvent, the polymeric material was dissolved in THF and poured into a large excess of methanol to precipitate. The in-chain-BnBr-functionalized PS-*block*-PMMA was purified by reprecipitation twice and freeze-drying from its absolute benzene solution under vacuum. The yield of the polymer was almost quantitative (1.37 g, 0.109 mmol, 92%). Both ^{1}H NMR and RALLS measurements showed that the SiOMP group was transformed cleanly and quantitatively into BnBr function. $M_{n,RALLS} = 12\,200$, $M_w/M_n = 1.03$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.09-6.58$ (broad, 289H, Ar), 4.29 (s, 2H, CH_2Br), 3.61 (s, 187H, OCH_3), 1.95−1.67 (broad, 199H, backbone), 0.77 (s, 175H, CCH_3).

General Procedure for Synthesis of Exact Graft Copolymers (EG-*n*). As mentioned above, both block copolymerization and linking reaction were carried out in THF under high-vacuum conditions (10^{-6} Torr) in a glass apparatus equipped with break-seals. Starting from the in-chain-BnBr-functionalized PS-*block*-PMMA above synthesized, a series of exact graft copolymers (EG-*n*, $n = 1, 2, 3, 4$) were synthesized by the iterative methodology that involves the following three reaction steps in each iterative reaction sequence: a block copolymerization of styrene and MMA to prepare in-chain-SiOMP-functionalized AB diblock copolymer (PS-*block*-PMMA) anion, a transformation reaction of the SiOMP group to BnBr function, and a coupling reaction of the BnBr function in the block copolymer with the above-mentioned in-chain-SiOMP-functionalized block copolymer anion. Both the preparation of the block copolymer anion and the transformation reaction were carried out according to the same procedure described preceding section.

In the linking reaction, a 2- or more excess of the in-chain-SiOMP-functionalized diblock copolymer anion was reacted with the in-chain-BnBr-functionalized graft copolymer at −40 °C for 24 h. After quenching the reaction with a small amount of degassed methanol, the reaction mixture was poured into a large excess of methanol to precipitate the polymers. SEC curve of the crude polymer showed two sharp peaks corresponding to the objective graft copolymer and the deactivated block copolymer anion used in excess. The reaction efficiency was always estimated by comparing the two SEC peak areas to be quantitative. The objective polymer was isolated by fractional precipitation using mixed solvents of THF, ether, and hexane as follows: The polymer was dissolved in a mixed solvent of THF/ether (2/100, v/v). Hexane was added slowly to the polymer solution until the solution became slightly cloudy. Then, the solution was kept at 0 °C for 1 h to precipitate the polymer(s). In general, high molecular weight objective graft copolymers were precipitated, while low molecular weight polymer anions deactivated remained in the solution. The graft copolymer was isolated in more than 80% yields in all cases by such a fractional precipitation procedure. The isolated polymer was reprecipitated from THF solution to methanol and freeze-dried from its absolute benzene solution for 2 days. The graft copolymer in-chain-functionalized with SiOMP group was characterized by RALLS and ^{1}H NMR in order to determine the absolute molecular weight, molecular weight distribution, composition ratio, and degree of in-chain-functionality.

Synthesis of Exact Graft Copolymers (EG-1). The in-chain-SiOMP-functionalized block copolymer anion was prepared by the block copolymerization of MMA (9.17 mmol) with living polystyrene (0.202 mmol, $M_n = 5830$) end-capped with **1** (0.267 mmol) in THF at −78 °C for 30 min in the presence of LiCl. Then, a THF (15.5 mL) solution of in-chain-BnBr-functionalized PS-*block*-PMMA (0.102 mmol for BnBr function, $M_n = 12\,600$) was added to the living polymer at −78 °C, and the reaction mixture was allowed to stand at −40 °C for 24 h. The linking reaction was terminated with degassed methanol. After usual work-up procedure, the EG-1 was isolated by fractional precipitation, reprecipitated from THF solution to methanol, and freeze-dried from its absolute benzene solution. $M_{n,RALLS} = 23\,600$, $M_w/M_n = 1.03$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.10-6.58$ (broad, 531H, Ar), 4.57 (m, 2H, CH_2O), 3.51 (s, 330H, OCH_3), 1.98−1.65 (broad, 299H, backbone), 0.76 (s, 280H, CCH_3), 0.08 (s, 6H, $Si(CH_3)_2$).

The in-chain-SiOMP-functionalized EG-1 (1.11 g, 0.0470 mmol for SiOMP group) was treated with LiBr (4.06 mmol) and $(CH_3)_3SiCl$ (4.06 mmol) in a mixed solvent of $CHCl_3/CH_3CN$ (25 mL/15 mL) at 40 °C for 24 h. The reaction was quenched with a small amount of methanol. After the work-up procedure mentioned above, the in-chain-BnBr-functionalized exact graft copolymer was obtained in a nearly quantitative yield (1.02 g, 0.0432 mmol, 92%). The quantitative transformation was confirmed by the observation that the signal assigned to benzyl protons was completely shifted from 4.57 ppm (CH_2O) to 4.25 ppm (CH_2Br) and that the disappearance of signals due to methyl protons of $Si(CH_3)_2$ at 0.08 ppm. The SEC analysis of the polymer showed that the monomodal sharp peak after the reaction was almost identical to that before the reaction. Thus, both ^{1}H NMR and RALLS measurements proved that the SiOMP group was transformed cleanly and quantitatively into BnBr function without any side reaction. $M_{n,RALLS} = 23\,300$, $M_w/M_n = 1.03$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.08-6.58$ (broad, 531H, Ar), 4.28 (s, 2H, CH_2Br), 3.60 (s, 330H, OCH_3), 1.96−1.63 (broad, 296H, backbone), 0.76 (s, 279H, CCH_3).

Synthesis of Exact Graft Copolymers with 2, 3, and 4 PS Grafts (EG-2, -3, and -4). The title exact graft copolymers were synthesized by the same iterative methodology as that employed for the synthesis of EG-1 mentioned above. The characterization results of EG-2, -3, and -4 are as follows: EG-2 (1.18 g, 0.0342 mmol, 80% yield), $M_{n,RALLS} = 34\,600$, $M_w/M_n = 1.02$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.08-6.58$ (broad, 825H, Ar), 4.59 (m, 2H, CH_2O), 3.60 (s, 539H, OCH_3), 2.08−1.65 (broad, 518H, backbone), 0.86 (s, 447H, CCH_3), 0.07 (s, 6H, $Si(CH_3)_2$). EG-3 (0.517 g, 0.0215 mmol, 82% yield), $M_{n,RALLS} = 45\,600$, $M_w/M_n = 1.04$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $d = 7.07-6.54$ (broad, 1095H, Ar), 4.56 (m, 2H, CH_2O), 3.61 (s, 691H, OCH_3), 1.96−1.63 (broad, 641H, backbone), 0.76 (s, 571H, CCH_3), 0.07 (s, 6H, $Si(CH_3)_2$). EG-4 (0.292 g, 0.0101 mmol, 86% yield), $M_{n,RALLS} = 55\,000$, $M_w/M_n = 1.04$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 6.98-6.57$ (broad, 1338H, Ar), 4.59 (m, 2H, CH_2O), 3.60 (s, 834H, OCH_3), 2.01−1.65 (broad, 840H, backbone), 0.76 (s, 821H, CCH_3), 0.02 (s, 6H, $Si(CH_3)_2$).

Synthesis of Exact Graft Copolymers (Block, EG′-1, EG′-2, and EG″-2). This series of exact graft copolymers was synthesized in the same manner as that described in the preceding section except for the use of three AB block copolymer anions with different molecular weights (PS (M_n)/PMMA (M_n) = 6100/6100, 2300/7700, and 6900/2800). Finally, a 1.5-fold excess of living PMMA ($M_n = 8400$) was coupled with the brominated EG′-2 under the same conditions to extend the backbone chain of EG′-2. The characterization results of these polymers are as follows: block, $M_{n,RALLS} = 12\,100$, $M_w/M_n = 1.03$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.08-6.59$ (broad, 303H, Ar), 4.55 (m, 2H, CH_2O), 3.60 (s, 189 H, OCH_3), 1.88−1.55 (broad, 156H, backbone), 0.86 (s, 216H, CCH_3), 0.03(s, 6H, $Si(CH_3)_2$); EG′-1 (4.58 g, 0.323 mmol, 86% yield), $M_{n,RALLS} = 23\,500$, $M_w/M_n = 1.03$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.07-6.57$ (broad, 463H, Ar), 4.62 (m, 2H, CH_2O), 3.60 (s, 433H, OCH_3), 2.03−1.64 (broad, 410H, backbone), 0.86 (s, 530H, CCH_3), 0.07 (s, 6H, $Si(CH_3)_2$); EG′-2 (2.70 g, 0.106 mmol, 80% yield), $M_{n,RALLS} = 33\,000$, $M_w/M_n = 1.04$. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): $\delta = 7.07-6.57$ (broad, 782H, Ar), 4.62 (m, 2H, CH_2O),

3.60 (s, 537H, OCH_3), 1.89−1.60 (broad, 602H, backbone), 0.85 (s, 673H, CCH_3), 0.02 (s, 6H, $Si(CH_3)_2$); EG″-2 (0.896 g, 0.0320 mmol, 83% yield), $M_{n,RALLS}$ = 42 100, M_w/M_n = 1.04. 300 MHz ^{1}H NMR ($CDCl_3$, ppm): δ = 7.07−6.57 (broad, 745H, Ar), 4.67 (m, 2H, CH_2O), 3.53 (s, 813H, OCH_3), 2.03−1.65 (broad, 837H, backbone), 0.85 (s, 985H, CCH_3), 0.02 (s, 6H, $Si(CH_3)_2$).

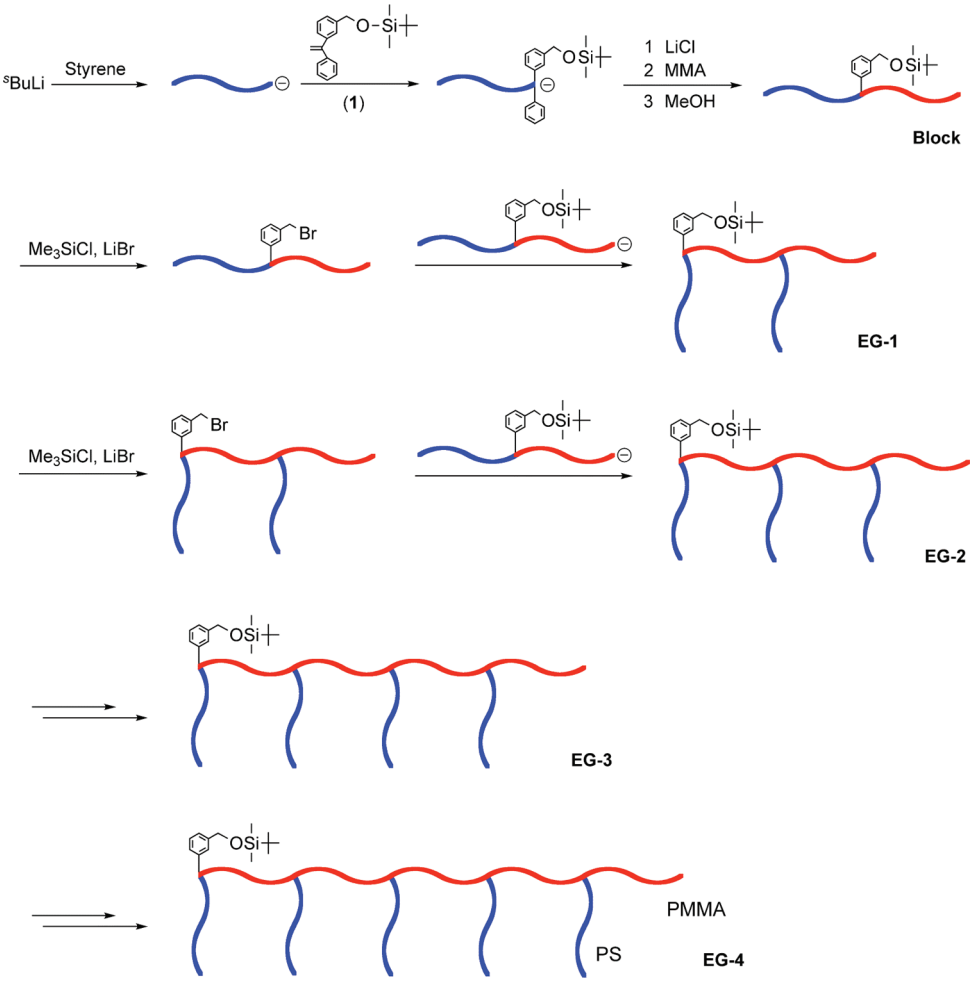
Results and Discussion

As mentioned in the Introduction, we have recently synthesized the well-defined exact comb (PS)s having up to five PS grafts by developing an iterative methodology.[8] As can be seen in Scheme 2, the backbone and graft chains are individually introduced in a stepwise fashion to construct one unit of graft polymer by each iterative reaction sequence. Herein, we have proposed a new conceptual iterative methodology for the synthesis of a series of exact graft copolymers composed of PMMA backbone chains and PS graft chains. The synthetic outline is illustrated in Scheme 3. In the present methodology, an in-chain-functionalized AB diblock copolymer (PS-*block*-PMMA) anion with SiOMP group between the PS and PMMA blocks is used as a key building block. This block copolymer anion is specially designed in order to simultaneously introduce both the backbone and graft chains to construct one graft unit via one coupling reaction step. The following three reaction steps are needed for the entire iterative reaction sequence: (1) a living anionic block copolymerization to prepare an in-chain-functionalized AB diblock copolymer (PS-*block*-PMMA) anion with SiOMP group between the PS and PMMA blocks, (2) a transformation of the SiOMP group to benzyl bromide (BnBr) function, and (3) a coupling reaction of the in-chain-BnBr-functionalized block polymer prepared by step 2 with the in-chain-SiOMP-functionalized block copolymer anion. Since the final polymer obtained by step 3 has the same SiOMP group introduced in the chain as the first starting material prepared by step 1, the same process involving the above reaction sequence can be repeated. Thus, the SiOMP group introduced in advance in the block copolymer plays an essential role to continue the iteration process.

In the first step of the iterative reaction sequence, the in-chain-SiOMP-functionalized AB diblock copolymer anion was prepared by the living anionic block copolymerization where styrene, **1**, and MMA were sequentially added in this order under the conditions in THF at −78 °C with *sec*-BuLi as an initiator. A 3-fold excess of LiCl to *sec*-BuLi was added prior to the polymerization of MMA in order to narrow the molecular weight distribution of the produced PMMA. Unless otherwise stated, the M_n value of the block copolymer (PS (M_n)/PMMA (M_n)) is adjusted to be around 10 000 g/mol (5000/5000). The block copolymer anion thus prepared was quenched with a small amount of degassed methanol, followed by treatment with a 1:1 mixture of $(CH_3)_3SiCl$ and LiBr to transform the SiOMP group to BnBr function.[12] Quantitative transformation was confirmed by the complete shift of the benzyl CH_2O−Si signal (4.56 ppm) to 4.29 ppm corresponding to methylene protons of the BnBr function as shown in Figure 1. In addition, the signal assigned to the silyl methyl protons at 0.17 ppm completely disappeared as observed in the same spectrum.

Then, the coupling reaction was carried out in THF at −40 °C for 24 h between the resulting in-chain-BnBr-functionalized AB

Scheme 3. Synthesis of a Series of Exact Graft Copolymers by Iterative Methodology



diblock copolymer and a 2.0-fold excess of in-chain-SiOMP-functionalized diblock copolymer anion separately prepared by the same manner. As shown in Figure 2, the SEC profile of the reaction mixture exhibited only two distinct sharp peaks. On the basis of their molecular weights, it was proved that a major high molecular weight peak corresponded to the objective coupled product, while a small low molecular weight peak was the excess deactivated block copolymer anion used in the reaction.

Similar to the coupling reaction previously reported,[13,14] the coupling efficiency was observed to be virtually quantitative by comparing the two peak areas. The coupled product isolated in 85% yield by fractional precipitation exhibited a narrow molecular weight distribution ($M_w/M_n = 1.03$) (see also Figure 2) and a M_n value that agreed well with the calculated value as listed in Table 1. The composition ratio of PS and PMMA segments observed by ^{1}H NMR was very close to that calculated from the both block copolymers. Accordingly, all of the analytical results

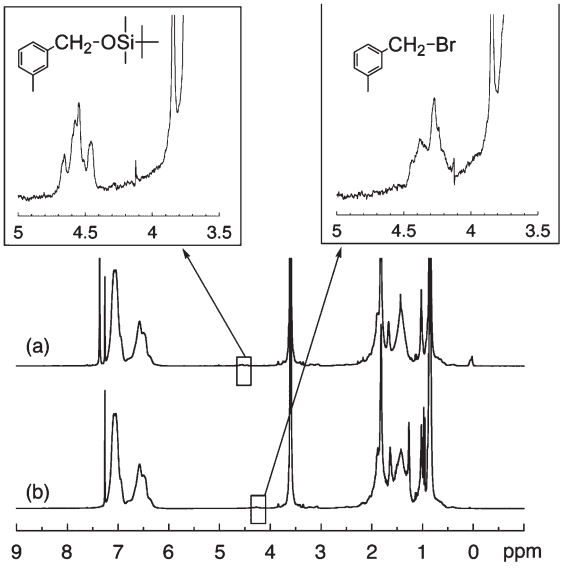


Figure 1. ^{1}H NMR spectra of in-chain-functionalized PS-*block*-PMMA with (a) SiOMP group and (b) BnBr function.

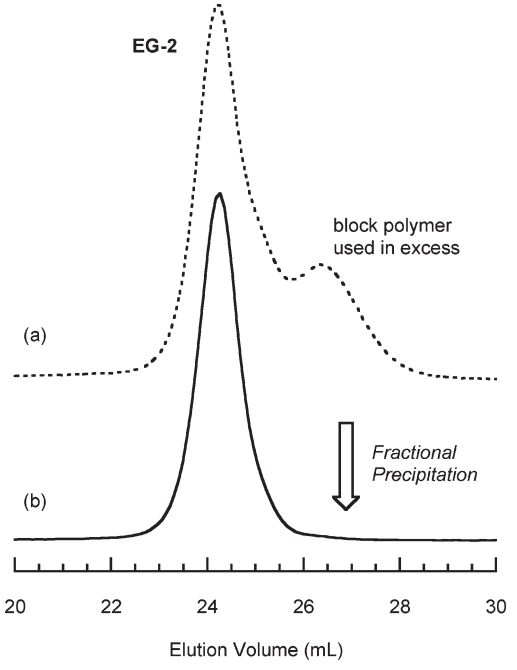


Figure 2. SEC profiles of exact graft copolymer (EG-2) (a) before and (b) after fractional precipitation.

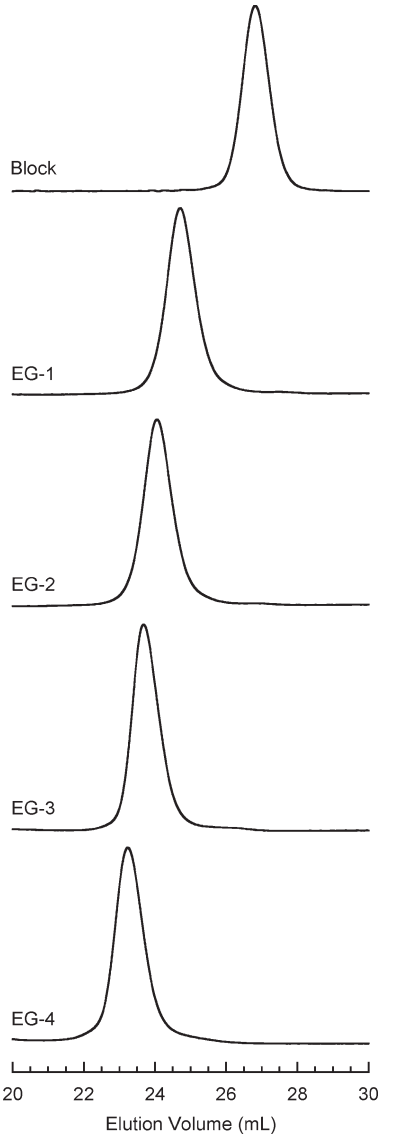


Figure 3. SEC curves for a series of exact graft copolymers and the starting block copolymer.

Table 1. Synthesis of a Series of Exact Graft Copolymers up to Five PS Grafts

	$M_n \times 10^{-3}$ (g/mol)				M_w/M_n	composition (PS/PMMA, wt/wt)	
code[a]	calcd	SEC[b]	NMR[c]	RALLS[d]	SEC[b]	calcd	obsd[c]
block[e]	12.5	11.7	12.6	12.6	1.03	50/50	48/52
EG-1	22.2	17.9	22.5	23.6	1.03	51/49	50/50
EG-2	33.8	31.9	35.4	34.6	1.02	50/50	49/51
EG-3	43.5	33.5	46.1	45.6	1.04	49/51	50/50
EG-4	56.2	41.3	56.0	55.0	1.04	50/50	50/50

[a] In-chain-SiOMP-functionalized exact graft copolymers. [b] Estimated by SEC with standard polystyrenes. [c] Determined by ^{1}H NMR. [d] Determined by SEC equipped with triple detectors. [e] The starting in-chain-SiOMP-functionalized block copolymer.

Scheme 4. Synthesis of Exact Graft Copolymers with Asymmetric Branched Structures

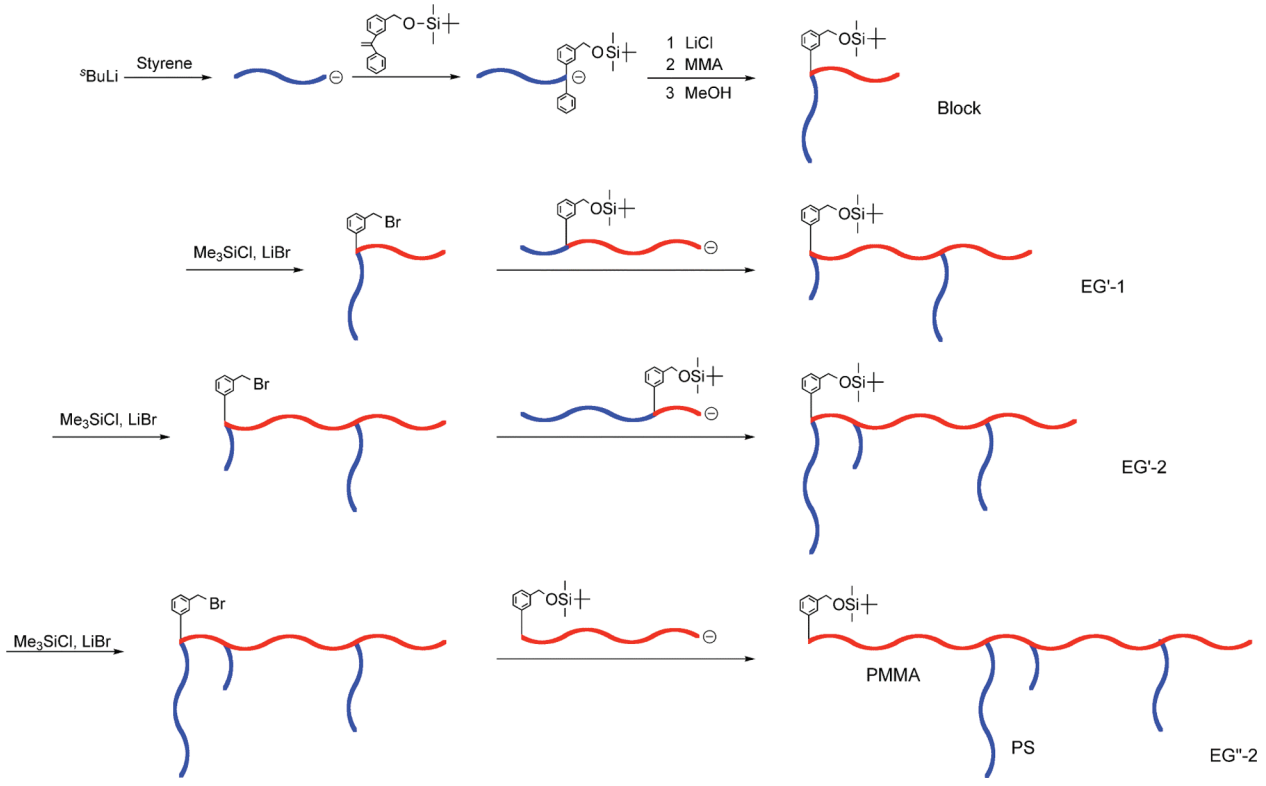


Table 2. Synthesis of Exact Graft Copolymers with Asymmetric Branched Structures

	$M_n \times 10^{-3}$ (g/mol)				M_w/M_n	composition (PS/PMMA, wt/wt)	
code[a]	calcd	SEC[b]	NMR[c]	RALLS[d]	SEC[b]	calcd	obsd[c]
block[e]	11.0	11.7	12.6	12.1	1.03	52/48	50/50
EG′-1	22.2	19.2	24.1	23.5	1.03	38/62	40/60
EG′-2	33.2	28.3	34.2	33.0	1.04	49/51	48/52
EG″-2[f]	41.4	33.0	42.6	42.1	1.04	38/62	36/64

[a] In-chain-SiOMP-functionalized exact graft copolymers. [b] Estimated by SEC with standard polystyrenes. [c] Determined by ^{1}H NMR. [d] Determined by SEC equipped with triple detectors. [e] The starting in-chain-SiOMP-functionalized block copolymer. [f] Exact graft copolymer with three PS graft chains obtained by the coupling reaction of EG′-2 with living PMMA.

clearly indicate that the coupling reaction efficiently proceeds to quantitatively afford an expected exact graft copolymers having two PS grafts referred to as EG-1.

Likewise, the graft copolymer having three PS grafts (EG-2) was synthesized by repeating the same reaction sequence (the second iterative process), which involved the bromination of EG-1 and the preparation of in-chain-SiOMP-functionalized AB diblock copolymer anion followed by the coupling reaction with the brominated EG-1. All of the three reaction steps were traced by ^{1}H NMR and SEC to observe the progress of the reactions under the same conditions. The successful formation of the EG-2 was confirmed by the characterization results listed in Table 1.

Since the EG-2 possessed the same SiOMP group at the chain-end as the EG-1, the same reaction sequence was further repeated two more times to synthesize graft copolymers having four and five PS graft chains (EG-3 and EG-4). All the reactions were monitored by SEC and found to proceed cleanly and quantitatively. Neither high molecular weight product nor the unreacted brominated polymer was observed at all in each case. The two graft copolymers isolated in ca. 80% yields by fractional precipitation and exhibited sharp monomodal SEC distributions. Agreement of the molecular weights as well as the compositions between calculated and observed was quite satisfactory in each of both samples.

Thus, obviously, the second, third, and fourth iterations work efficiently without any difficulty to afford the objective well-defined exact graft copolymers having three, four, and so on to five PS grafts. Figure 3 shows the SEC peaks of all the isolated exact graft copolymers from EG-1 to EG-4 in addition to the starting AB diblock copolymer. As you can see, these polymers possess sharp monomodal distributions without shoulders or tailings.

In order to demonstrate the possible control of the distance between the branch points as well as the molecular weight of PS graft chain, three in-chain-functionalized AB block copolymer anions having different compositions (PS (M_n)/PMMA (M_n): 6100/6100, 2300/7700, and 6900/2800) were prepared and sequentially coupled in the same manner as illustrated in Scheme 4.

In this polymer series (EG′-1 and EG′-2), living PMMA (M_n = 8400 g/mol) was finally coupled with the brominated EG′-2 to extend the backbone chain. It was roughly estimated from the SEC profiles that all of the coupling reactions proceeded quantitatively. The two graft copolymers, EG′-1 and EG′-2, as well as the final product (EG″-2) were isolated in ca. 70% yields by fractional precipitation and analyzed by ^{1}H NMR, SEC, and RALLS. The characterization results listed in Table 2 clearly indicate the successful formation of the objective exact graft copolymers with well-defined and expected structures. Thus, the distance between junction points and the molecular weight of

graft chains were readily controlled by changing the composition of AB diblock copolymer anion.

In the present methodology herein developed, the iterative reaction sequence involving the three reaction steps works satisfactorily at least four times to successively synthesize a series of well-defined exact graft copolymers with up to five PS grafts. Throughout the synthesis of the exact graft polymer series, the specially designed in-chain-SiOMP-functionalized AB block copolymer anion proves to play an essential role as a key building block. Importantly and interestingly, both the backbone and graft chains are simultaneously introduced to construct one graft at once unit via the coupling reaction step with this AB block copolymer anion. This is a big conceptual difference between the present methodology and our previous methodology where the backbone and graft chains are individually introduced in a stepwise fashion (see Scheme 2). Moreover, it should be mentioned that the series of exact graft polymers composed of PMMA backbones and PS grafts herein synthesized cannot be synthesized by the previous methodology. Thus, the excellence as well as novelty of the present iterative methodology using the AB diblock copolymer anion has been demonstrated. The choice and setting of the three reaction conditions used in the reaction sequence are essential to achieve the successive synthesis by repeating the reaction sequence. Needless to say, the reaction inefficiencies and accidental mixing of impurities do not allow synthesizing such a series of well-defined graft copolymers. As can be seen in Scheme 3, the final product of EG-4 has the same SiOMP group in the polymer chain, and therefore, the same process will be repeated to further synthesize the exact graft copolymers having six or more graft chains.

Conclusions

We have successfully developed the iterative methodology based on a new concept using an in-chain-SiOMP-functionalized AB diblock copolymer anion for the synthesis of exact graft copolymers composed of PMMA backbone chains and PS graft chains. The methodology involves only three reaction steps mentioned above in the entire iterative reaction sequence. By repeating the reaction sequence five times, a series of exact graft copolymers composed of PMMA backbones and PS grafts up to five in number have been successively synthesized. In the graft copolymers thus synthesized, all of the four parameters required for exact graft copolymer are perfectly controlled. Since it may be possible to prepare in-chain-functionalized AB diblock copolymers composed of various functional methacrylate polymer segments as the B blocks, a variety of methacrylate polymers with useful functionalities can be introduced as the backbone chains of exact graft copolymers instead of PMMA segment. This is now under investigation.

Acknowledgment. A.H. gratefully acknowledges partial support by a grant (B: 21350060) from a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan. A.H. is also thankful for the financial support from Denki Chemical Co. Ltd. K.S. thanks for a partial support from a JSPS Grants-in-Aid for Scientific Research (C: 21550114).

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