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General and Facile Approach to Exact Graft Copolymers by Iterative Methodology Using Living Anionic In-Chain-Functionalized AB Diblock Copolymers as Key Building Blocks

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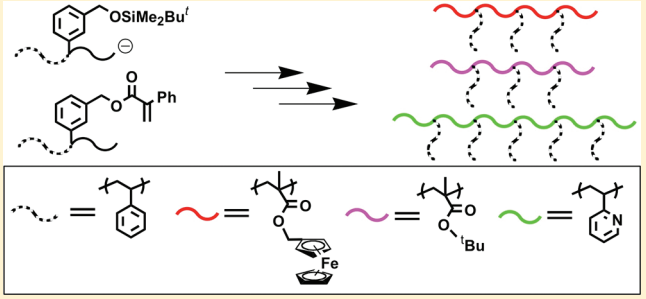
ABSTRACT: A variety of exact graft copolymers, such as poly(*tert*-butyl methacrylate)-*exact graft*-polystyrene (PS), poly(ferrocenylmethyl methacrylate)-*exact graft*-PS, and poly(2-vinylpyridine)-*exact graft*-PS, have been successfully synthesized by developing a novel stepwise iterative methodology based on a new concept utilizing living in-chain-(3-*tert*-butyldimethylsilyloxymethylphenyl) (SiOMP)-functionalized AB diblock copolymers as key building blocks. The methodology basically involves three reaction steps in each iterative process, i.e., (1) living anionic block copolymerization to prepare a living in-chain-SiOMP-functionalized AB diblock copolymer, (2) a transformation reaction of the SiOMP group into an α-phenyl acrylate (PA) function, and (3) a 1:1-addition reaction of the resulting in-chain-PA-functionalized AB diblock copolymer with a living in-chain-SiOMP-functionalized AB diblock copolymer separately prepared to link the two block copolymer chains. By performing the same iterative process involving steps 1−3 several times, the above-mentioned exact graft copolymers having three to five PS branches were synthesized. The resulting polymers were all well-defined in architecture and precisely controlled in chain structure.



INTRODUCTION

Graft (co)polymers have long been known as one of the representative branched polymers and widely studied because of their unique and interesting properties, behavior, and morphologies in solution as well as bulk.[1−7,10c,10e] As shown in Figure 1, the structure of a graft (co)polymer is defined by the following four parameters: (1) molecular weight of the backbone chain, (2) molecular weight of the graft chain, (3) distance between graft chains, and (4) the number of branch points along the backbone chain. In particular, it is important that the parameters of each branch chain can be controlled, e.g., different branching distances, lengths of graft chains, and number of branch point. An ideal graft (co)polymer, in which all of the four parameters are perfectly controlled, is called "an exact graft (co)polymer" by Hadjichristidis.[8] Although several attempts have been made to synthesize such ideal graft copolymers, most of those so far synthesized have not been completely controlled with respect to the above four parameters.[9−11]

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 developing a new stepwise iterative methodology, as shown in Scheme 1.[8] The first step was an addition reaction of poly(isoprenyl)lithium (PILi) to 1,4-bis(phenylethenyl)benzene to introduce the 1,1-diphenylethylene (DPE) function at the chain end. The resulting ω-terminal DPE-functionalized PI was then reacted with a stoichiometric amount of polystyryllithium (PSLi) in a 1:1 addition manner to link PS to the PI chain in the second step. The thus-formed AB diblock copolymer with a DPE-derived anion generated between the two chains was used *in situ* as a macroinitiator in the polymerization of isoprene to prepare a living 3-arm AA'B star-branched polymer. By repeating the same reaction steps, the target exact graft copolymer having two PS graft chains was successfully synthesized. As you can see, all four parameters are controlled by the molecular weights of the living anionic PI and PS chains. Hadjichristidis and his coworkers also synthesized an exact graft poly(1,3-butadiene) (PB) (or an exact comb PB) having three PB graft chains by using the intermediate polymers produced in the above methodology with a combination of DPE and chlorosilane chemistry.[12]

The methodology can offer potential for providing a general procedure for exact graft (co)polymers with more graft chains by performing the same iterative process. However, the synthesis may be significantly limited because a perfect 1:1 stoichiometry, experimentally very difficult, is always required in each addition reaction of PSLi to the DPE function in the polymer chain.

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Recently, we developed an improved methodology using premade living polymers in conjunction with specially designed termination reactions, by which a 1:1 stoichiometry in the reaction is avoided to successfully synthesize a series of exact graft (PS)s having up to five PS branch chains.[13]

In order to explore a more efficient methodology for the synthesis of exact graft copolymers, we recently proposed a novel stepwise iterative methodology based on a new concept utilizing living in-chain-functionalized AB diblock copolymers as the key building blocks, as illustrated in Scheme 2.[14,15] In this methodology, the following three reaction steps were employed in each iterative process: (1) living anionic block copolymerization to prepare the living in-chain-(3-*tert*-butyldimethylsilyloxymethylphenyl) (SiOMP)-functionalized PS-*block*-PMMA, (2) a transformation reaction of the introduced SiOMP group into a benzyl bromide (BnBr) function used as the reaction site, and (3) a coupling reaction of the resulting in-chain-BnBr-functionalized PS-*block*-PMMA with a living in-chain-SiOMP-functionalized PS-*block*-PMMA separately prepared. Since the three reaction steps quantitatively proceeded, they could be repeated four more times to result in a series of exact graft copolymers composed of PMMA backbone chains and up to five PS graft chains. In the resulting polymers, the lengths of the PS-graft chains and their distance can be individually adjusted. The number of branch points is determined by the number of iterative processes involving the three reaction steps. Thus, the resulting polymers were all well-defined with respect to the above-mentioned four parameters. Furthermore, with this methodology utilizing AB diblock copolymers instead of a living single polymer chain, the number of reaction steps required for synthesis can be basically reduced by half and a series of new exact graft copolymers synthetically difficult can be synthesized.

Herein, we report on the extension of this novel stepwise iterative methodology to a more general and versatile methodology, in which the α-phenyl acrylate function is adopted as a new reaction site for the synthesis of a variety of exact graft copolymers.

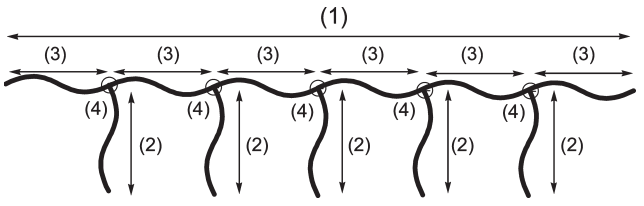


Figure 1. Exact graft copolymer, in which all four parameters are perfectly controlled.

EXPERIMENTAL SECTION

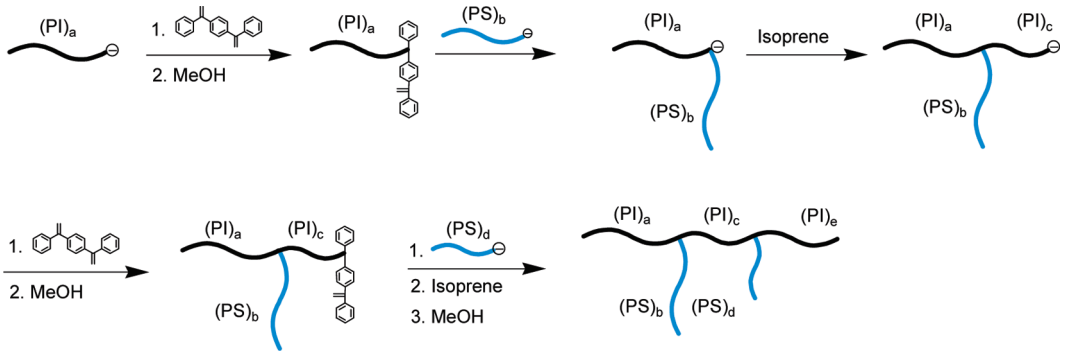
Materials. The reagents (>98% purities) were purchased from Aldrich Japan and used as received unless otherwise stated. Styrene, 1,1-diphenylethylene (DPE), *tert*-butyl methacrylate (^{t}BMA), methyl methacrylate (MMA), 2-perfluorooctylethyl methacrylate (F_8H_2-MA) (>98%, Wako Pure Chemicals, Co., Ltd., Japan), 2-vinylpyridine, and *N*,*N*-diethyl acrylamide, THF, chloroform, acetonitrile, $(CH_3)_3SiCl$, LiCl, and LiBr were purified according to the reported procedures described elsewhere.[13,14,16] Ferrocenylmethyl methacrylate (FMMA) was synthesized according to the reported procedure.[17]

Styrene was finally distilled in the presence of Bu_2Mg (*ca.* 3 mol %) on the vacuum line. Both ^{t}BMA and MMA was finally distilled from their 3 mol % $(C_6H_{13})_3Al$ solution on the vacuum line. 2-Vinylpyridine, F_8H_2-MA, and *N*,*N*-diethyl acrylamide were finally distilled over fine powder CaH_2 (after stirring for a few hours) twice on the vacuum line. 3-Hydroxy-2-phenylpropanoic acid, $(C_4H_9)_4NF$ (1.0 M solution in THF), triphenylphosphine (PPh_3), and diisopropyl azodicarboxylate (DIAD) were purchased from Tokyo Kasei Kogyo Co., Ltd., Japan, and used as received. 1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-phenylethylene (**1**) was synthesized according to our procedure previously reported.[16] α-Phenylacrylic acid was synthesized by the procedure previously reported.[18]

Measurements. Both ^{1}H 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 ^{1}H 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 columns (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 diblock copolymers, and branched polymers.

General Procedure for Synthesis of Exact Graft Copolymers. All of the exact graft copolymers herein synthesized were obtained by performing the iterative process including three reaction steps using the corresponding living in-chain-SiOMP-functionalized AB diblock copolymers as the building blocks. In the last iteration, a living polymer of ^{t}BMA, FMMA, or 2VP was reacted with the terminal PA function of the backbone chain to introduce an extra chain into the backbone chain at the other side. The three reaction steps in the iterative process were carried out in the same manner as those described above. The amount of the living in-chain-SiOMP-functionalized AB diblock copolymer was gradually increased from a 2-fold excess to a 4-fold excess for the PA function with increasing

Scheme 1. Synthesis of Exact Graft Copolymer Composed of PI and PS Segments



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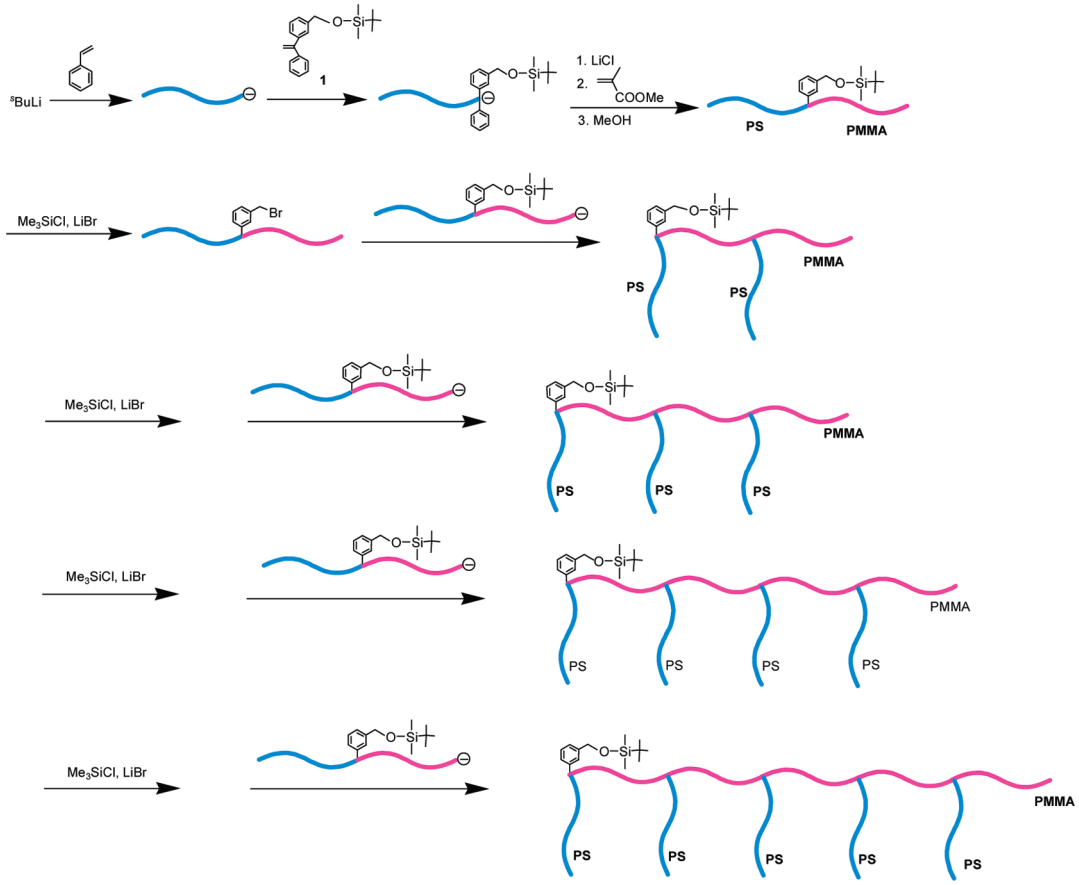
Scheme 2. Synthesis of Exact Graft Copolymers Composed of PMMA and PS Segments by Novel Iterative Methodology



the iteration in number in order to force the addition reaction to completion. The resulting polymers were isolated in 40−80% yields by fractional precipitation using a combination of good (or poor) and nonsolvents. The isolated polymers by this fractionation were often included small amounts (3−15%) of unreacted AB diblock copolymers. In such cases, pure polymer samples were obtained by the fractionation with SEC and characterized by ^{1}H NMR, SEC, and SEC-RALLS. The synthesis of a P^{t}BMA-*exact graft*-PS having three PS graft chains is described as a typical example.

Preparation of Living In-Chain-SiOMP-Functionalized PS-*block*-P^{t}BMA. All polymerizations and addition reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors equipped with break-seals. All reactors were prewashed with red-colored 1,1-diphenylhexyllithium (*ca.* 0.05 M) in heptane after being sealed off from a vacuum line and used.

Styrene (9.25 mmol) in THF solution (9.33 mL) precooled at −78 °C was added at once with shaking to *sec*-BuLi (0.187 mmol) in heptane solution (2.40 mL) at −78 °C, and the polymerization was allowed to stand at −78 °C for 20 min. Then, **1** (0.308 mmol) in THF solution (5.45 mL) was added to the resulting polystyryllithium (PSLi) at −78 °C and the reaction mixture was allowed to stand for additional 0.5 h. After the addition of LiCl (0.935 mmol) dissolved in THF (3.11 mL), ^{t}BMA (7.35 mmol) in THF solution (6.94 mL) was added to polymerize it in THF at −78 °C for 1.5 h. The polymer was quenched with degassed methanol and precipitated in a large amount of methanol. It was reprecipitated twice from THF to methanol, and freeze-dried from its dry benzene solution in vacuo for 24 h. The polymer (2.03 g) was obtained in 99% yield and characterized by SEC, SEC-RALLS, and ^{1}H NMR. ^{1}H NMR ($CDCl_3$): δ 7.43−6.15 (m, aromatic), 4.62 (s, Ph−CH_2−O−Si), 2.60−0.73 (m, −CH_2−C(CH_3)- and −CH_2−CH−), 1.44 (s, −C(CH_3)$_3$), 0.01 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 10 900 g/mol; M_w/M_n = 1.03.

Preparation of In-Chain-PA-Functionalized PS-*block*-P^{t}BMA. Under an atmosphere of nitrogen, the resulting in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA (1.83 g, 0.168 mmol for the SiOMP group) dissolved in THF (20.0 mL), was mixed with $(C_4H_9)_4NF$ (5.00 mmol) in THF (5.00 mL) at 0 °C. The reaction mixture was allowed to stand at 0 °C for additional 6 h. After quenching with a small amount of degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was purified by reprecipitation twice from THF to methanol and freeze-dried from its absolute benzene solution (1.75 g, 97%). ^{1}H NMR ($CDCl_3$): δ 7.42−6.13 (m, aromatic), 4.61 (s, Ph−CH_2−O−H), 2.63−0.74 (m, −CH_2−C(CH_3)− and −CH_2−CH−), 1.44 (s, −C(CH_3)$_3$).

Under nitrogen, the resulting polymer (1.65 g, 0.153 mmol for the OH group), dissolved in absolute THF (20.0 mL), was mixed with α-phenyl acrylic acid (7.32 mmol) and PPh_3 (7.32 mmol), followed by the subsequent addition of DIAD (10.9 mmol) dissolved in absolute THF (10.0 mL) to the reaction mixture at 0 °C. The reaction mixture was allowed to stand at 25 °C for 24 h. After quenching with a small amount of degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was purified by reprecipitation twice from THF to methanol and freeze-drying from its absolute benzene solution for 24 h, resulting in the target in-chain-PA−functionalized PS-*block*-P^{t}BMA (1.52 g, 91%). ^{1}H NMR ($CDCl_3$): δ 7.44−6.13 (m, aromatic), 5.86 (s, C═CH_2), 5.06 (s, Ph−CH_2−O−C(═O)), 2.60−0.73 (m, −CH_2−C(CH_3)− and −CH_2−CH−), 1.43 (s, −C(CH_3)$_3$).

Synthesis of Exact Graft Copolymer Precursor Having Two PS Graft Chains (EG′(^{t}BMS)-2). A THF (16.5 mL) solution of

in-chain-PA-functionalized PS-*block*-P^{t}BMA (1.40 g, 0.127 mmol for PA function), precooled at −78 °C, was added to the living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA (0.260 mmol for the chain-end enolate anion, M_n(SEC-RALSS) = 9300 g/mol) end-capped with MMA (1.25 mmol) in THF (1.40 mmol) at −78 °C for 30 min. The reaction mixture was allowed to stand at −40 °C for 24 h. The reaction was terminated by a small amount of degassed methanol and poured into a large amount of methanol to precipitate the polymers. After the polymer mixture was characterized by SEC, the polymers were first fractionated by a mixed solvent of methanol and acetone to isolate the 1:1 addition product (target polymer) in 88% yield. A small amount (∼5%) of the deactivated starting living diblock copolymer was contaminated in the isolated polymer sample. A pure polymer sample was obtained by SEC fractionation and purified by reprecipitation twice, followed by freeze-drying from its absolute benzene solution for 24 h. It was characterized by SEC, SEC-RALLS, and ^{1}H NMR analyses. ^{1}H NMR ($CDCl_3$): δ 7.43−6.15 (m, aromatic), 5.16−4.51 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 3.60 (s, O−CH_3), (s, 2.60−0.73 (m, −CH_2−C(CH_3)− and −CH_2−CH−), 1.44 (s, −C(CH_3)$_3$), 0.01 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 20 300 g/mol; M_w/M_n(SEC) = 1.04.

Synthesis of Exact Graft Copolymer Precursor Having Three PS Graft Chains (EG′(tBMS)-3). The title polymer was synthesized by performing the iterative process under exactly the same conditions as those mentioned above. A living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA (M_n = 9800 g/mol) was used in a 3-fold molar excess for the PA function. The three reactions efficiently proceeded to afford the expected exact graft copolymer precursor having three PS graft chains. The target polymer was isolated by fractionation using a mixture of acetone and methanol, followed by the fractionation with SEC (2.29 g, 50% yield). ^{1}H NMR ($CDCl_3$): δ 7.45−6.12 (m, aromatic), 5.16−4.46 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 3.59 (s, O−CH_3), 2.61−0.71 (m, −CH_2−C(CH_3)- and −CH_2−CH-), 1.42 (s, −C(CH_3)$_3$), −0.02 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 30 900 g/mol; M_w/M_n(SEC) = 1.04.

Synthesis of Exact Graft Copolymer Composed of a P^{t}BMA Backbone and Three PS Chains (EG(tBMS)-3). The resulting polymer obtained as above was treated with Bu_4NF, followed by the Mitsunobu esterification reaction with α-phenylacrylic acid, to transform the SiOMP group into the PA function. Then, a living P^{t}BMA was prepared at −78 °C for 5 h by the living anionic polymerization of ^{t}BMA (5.10 mmol) with the initiator prepared from *sec*-BuLi (0.178 mmol) and **1** (0.271 mmol) in the presence of LiCl (0.724 mmol) (total 15.5 mL THF solution) and end-capped with MMA (0.788 mmol) in THF solution (1.02 mL). It was reacted with the PA-functionalized precursor polymer (1.73 g, 0.0560 mmol for PA group) dissolved in THF (17.9 mL) at −40 °C for 24 h. After the usual work-up, the target exact graft copolymer having three PS graft chains was isolated in 40% yield (0.782 g) by fractional precipitation using methanol and acetone. ^{1}H NMR ($CDCl_3$): δ 7.46−6.15 (m, aromatic), 5.16−4.48 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 3.60 (s, O−CH_3), 2.65−0.75 (m, −CH_2−C(CH_3)− and −CH_2−CH−), 1.41 (s, −C(CH_3)$_3$), 0.04 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 34 800 g/mol; M_w/M_n(SEC) = 1.05.

Synthesis of Exact Graft Copolymers Composed of a PFMMA Backbone and Three PS Chains (EG(FMS)-3) and a P2VP Backbone and Five PS Chains (EG(PyS)-5). A series of exact graft copolymers, PFMMA-*exact graft*-PS and P2VP-*exact graft*-PS, were synthesized by the similar procedures described in the general procedure mentioned above. The linking reaction between living PS-*block*-PFMMA and the in-chain-PA-functionalized polymer was carried out at −40 °C for 24 h, while living PS-*block*-P2VP always reacted with the in-chain-PA-functionalized polymer at −78 °C for 24 h. An excess (2−3 times) of living polymer toward the PA reaction site was used to complete the linking reaction. The reactions were terminated at −78 °C with degassed methanol. These copolymers were isolated by fractional precipitation using ethanol/hexane for PFMMA-*exact graft*-PS and THF/methanol for P2VP-*exact graft*-PS, respectively. Finally, pure polymer samples were obtained by the fractionation with SEC. Their characterization results are as follows: The resulting exact graft copolymers and copolymer precursors having *n* PS graft chains are abbreviated as EG(FMS or PyS)-*n* and EG′(FMS or PyS)-*n*, respectively.

PFMMA-*exact graft*-PS (EG(FMS)-*n*). In-chain-SiOMP-functionalized PS-*block*-PFMMA. ^{1}H NMR ($CDCl_3$): δ 7.32−6.13 (m, aromatic), 4.84−4.52 (m, Ph−CH_2−O−Si and Ph−CH_2−O−ferrocene (Fc)), 4.08 (s, C_5H_5 of Fc), 2.28−0.32 (m, −CH_2−C(CH_3)− and −CH_2−CH−), −0.01 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 11 900 g/mol; M_w/M_n(SEC) = 1.03. In-chain-OH-functionalized PS-*block*-PFMMA. ^{1}H NMR ($CDCl_3$): δ 7.33−6.13 (m, aromatic), 4.83−4.51 (m, Ph−CH_2−OH and Ph−CH_2−O−ferrocene (Fc)), 4.08 (s, C_5H_5 of Fc), 2.25−0.31 (m, −CH_2−C(CH_3)− and −CH_2−CH−). In-chain-PA-functionalized PS-*block*-PFMMA. ^{1}H NMR ($CDCl_3$): δ 7.31−6.10 (m, aromatic), 5.75 (s, C=CH_2), 4.99−4.51 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−ferrocene (Fc)), 4.06 (s, C_5H_5 of Fc), 2.26−0.31 (m, −CH_2−C(CH_3)- and −CH_2−CH−). EG′(FMS)-2. ^{1}H NMR ($CDCl_3$): δ 7.30−6.12 (m, aromatic), 4.99−4.51 (m, Ph−CH_2−O−C(=O), Ph−CH_2−O−Si, and Ph−CH_2−O−ferrocene (Fc)), 4.04 (s, C_5H_5 of Fc), 2.32−0.38 (m, −CH_2−C(CH_3)- and −CH_2−CH−), −0.02 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 21 000 g/mol; M_w/M_n(SEC) = 1.03. EG′(FMS)-3. ^{1}H NMR ($CDCl_3$): δ. 7.34−6.12 (m, aromatic), 4.99−4.50 (m, Ph−CH_2−O−C(=O), Ph−CH_2−O−Si), and Ph−CH_2−O−ferrocene (Fc)), 4.02 (s, C_5H_5 of Fc), 2.30−0.31 (m, −CH_2−C(CH_3)−, and −CH_2−CH−), −0.04 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 33 000 g/mol; M_w/M_n(SEC) = 1.04. EG(FMS)-3. ^{1}H NMR ($CDCl_3$): δ. 7.31−6.08 (m, aromatic), 4.99−4.51 (m, Ph−CH_2−O−C(=O), Ph−CH_2−O−Si, and Ph−CH_2−O−ferrocene (Fc)), 4.01 (s, C_5H_5 of Fc), 2.31−0.32 (m, −CH_2−C(CH_3)− and −CH_2−CH−). M_n(SEC-RALLS) = 39 200 g/mol; M_w/M_n(SEC) = 1.04.

P2VP-*exact graft*-PS (EG(PyS)-*n*). In-chain-SiOMP-functionalized PS-*block*-P2VP. ^{1}H NMR ($CDCl_3$): δ 8.56−8.03 (m, −NCH=), 7.59−6.12 (m, aromatic), 4.46 (s, Ph−CH_2−O−Si), 2.48−1.31 (m, −CH_2−CH−), 0.06 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 10 600 g/mol; M_w/M_n(SEC) = 1.03. In-chain−OH-functionalized PS-*block*-P2VP. ^{1}H NMR ($CDCl_3$): δ 8.56−8.03 (m, −NCH=), 7.59−6.12 (m, aromatic), 4.46 (s, Ph−CH_2−OH), 2.48−1.31 (m, −CH_2−CH−). In-chain-PA-functionalized PS-*block*-P2VP. ^{1}H NMR ($CDCl_3$): δ 8.52−8.05 (m, −NCH=), 7.52−6.08 (m, aromatic), 5.71 (s, C=CH_2), 4.99 (s, Ph−CH_2−O−C(=O)), 2.51−1.37 (m, −CH_2−CH−). EG′(PyS)-2. ^{1}H NMR ($CDCl_3$): δ 8.52−8.06 (m, −NCH=), 7.56−6.12 (m, aromatic), 5.09−4.39 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 2.48−1.30 (m, −CH_2−CH−), 0.01 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 20 100 g/mol; M_w/M_n(SEC) = 1.04. EG′(PyS)-3. ^{1}H NMR ($CDCl_3$): δ 8.51−8.10 (m, −NCH=), 7.56−6.11 (m, aromatic), 5.09−4.38 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 2.52−1.30 (m, −CH_2−CH−), −0.02 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 31 100 g/mol; M_w/M_n(SEC) = 1.05. EG′(PyS)-4. ^{1}H NMR ($CDCl_3$): δ 8.52−8.12 (m, −NCH=), 7.52−6.10 (m, aromatic), 5.09−4.39 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 2.50−1.31 (m, −CH_2−CH−), −0.02 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 39 800 g/mol; M_w/M_n(SEC) = 1.05. EG′(PyS)-5. ^{1}H NMR ($CDCl_3$): δ 8.54−8.13 (m, −NCH=), 7.54−6.11 (m, aromatic), 5.09−4.39 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 2.53−1.34 (m, −CH_2−CH−), 0.02 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 49 100 g/mol; M_w/M_n(SEC) = 1.04. EG(PyS)-5. ^{1}H NMR ($CDCl_3$): δ 8.53−8.11 (m, −NCH=), 7.55−6.10 (m, aromatic), 5.09−4.39 (m, Ph−CH_2−O−C(=O) and Ph−CH_2−O−Si), 2.52−1.26 (m, −CH_2−CH−), −0.04 (s, Si(CH_3)$_2$). M_n(SEC-RALLS) = 54 500 g/mol; M_w/M_n(SEC) = 1.06.

Synthesis of Exact Graft Copolymer Precursor Composed of a P(F8H2-MA) Backbone and Two PS Chains. Living in-chain-SiOMP-functionalized PS-*block*-P(F8H2-MA) was prepared by the

living anionic block polymerization where styrene, **1**, and F8H2-MA were added to *sec*-BuLi in the presence of LiCl in THF at −78 °C, similar to the synthesis of living in-chain-SiOMP-functionalized PS-*block*-PMMA as mentioned above. The SiOMP group was converted to a PA reaction site by treatment with $(C_4H_9)_4NF$ and subsequently with α-phenylacrylic acid under the same conditions. The resulting in-chain-PA-functionalized PS-*block*-P(F8M2-MA) (M_n = 10 200 g/mol; M_w/M_n = 1.07, 52/48 (w/w)) was reacted with a 3-fold excess of living in-chain-SiOMP-functionalized PS-*block*-P(F8H2-MA) (M_n = 9700 g/mol; M_w/M_n = 1.10, 50/50 (w/w)) in THF at −40 °C for 24 h. After termination with degassed methanol, the polymers were precipitated in methanol. The SEC profile of the polymer mixture showed two peaks overlapped to each other to a certain extent. The reaction efficiency was estimated to be nearly quantitatively by comparing these peak areas. The target polymer was isolated by the SEC fractionation. ^{1}H NMR ($CDCl_3$): δ 7.07−6.50 (m, aromatic), 4.29 (s, $-OCH_2$-CH_2-), 2.44 (s, $-OCH_2-CH_2-$), 2.32−1.26 (m, $-CH_2-CH-$). M_n(SEC-RALLS) = 20 500 g/mol; M_w/M_n(SEC) = 1.26.

Synthetic Attempt of Exact Graft Copolymer Precursor Composed of a Poly(*N,N*-diethyl acrylamide) (PAA) Backbone and Two PS Chains. The in-chain-SiOMP-functionalized PS-*block*-PAA was prepared by the living anionic polymerization where styrene, **1**, and *N,N*-diethyl acrylamide were sequentially added to Ph_2CHLi and Et_2Zn in THF at −78 °C. The resulting polymer was treated with $(C_4H_9)_4NF$ and subsequently with α-phenylacrylic acid under the same conditions. ^{1}H NMR ($CDCl_3$): δ 7.35−6.10 (m, aromatic), 5.75 (s, C=CH*H*), 4.85 (s, $-OCHH_2-$), 2.44 (s, $-OCHH_2-CH_2-$), 3.31 (s, N−$OCHH_2-$), 2.76 (s, $-OCHH_2-CH_3$), 2.10−0.55 (m, $-CH_2-CH-$). M_n(SEC-RALLS) = 10 500 g/mol; M_w/M_n(SEC) = 1.05. Composition: 50/50 (w/w)).

A 3-fold excess of living in-chain-SiOMP-functionalized PS-*block*-PAA (M_n = 10 300 g/mol; M_w/M_n(SEC) = 1.05. 51/49 (w/w)) was newly prepared and reacted with the in-chain-PA-functionalized PS-*block*-PAA in THF at −40 °C for 24 h. The SEC profile of the reaction mixture showed only one peak eluted at the same count as that for each of both block copolymers.

RESULTS AND DISCUSSION

Synthesis of Exact Graft Copolymers Composed of P^{t}BMA and PS Segments (P^{t}BMA-*exact graft*-PS). We first attempted to synthesize a P^{t}BMA-*exact graft*-PS by developing the same methodology as that employed for the successful synthesis of the series of (PMMA-*exact graft*-PS)s mentioned in the Introduction.[14] Similar to the preparation of living anionic in-chain-SiOMP-functionalized PS-*block*-PMMA, a living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA was readily prepared by living anionic block copolymerization, where styrene, 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene (**1**), and ^{t}BMA were sequentially added to *sec*-BuLi in this order. Needless to say, the DPE derivative, **1**, underwent a 1:1 addition reaction to introduce the SiOMP group at the PS chain-end. Subsequently, ^{t}BMA was *in situ* polymerized with the generated DPE-derived anion to place the SiOMP group at a position between the PS and P^{t}BMA blocks. After termination, the SiOMP group was treated with a 1:1 mixture of Me_3SiCl and LiBr in order to transform it into a BnBr function. However, unfortunately, not only the transformation reaction, but also the acid-labile *tert*-butyl ester cleavage of P^{t}BMA simultaneously occurred by this treatment. Even under mild conditions, the cleavage could not be avoided. Thus, the transformation reaction with Me_3SiCl and LiBr was not useful in the PS-*block*-P^{t}BMA.

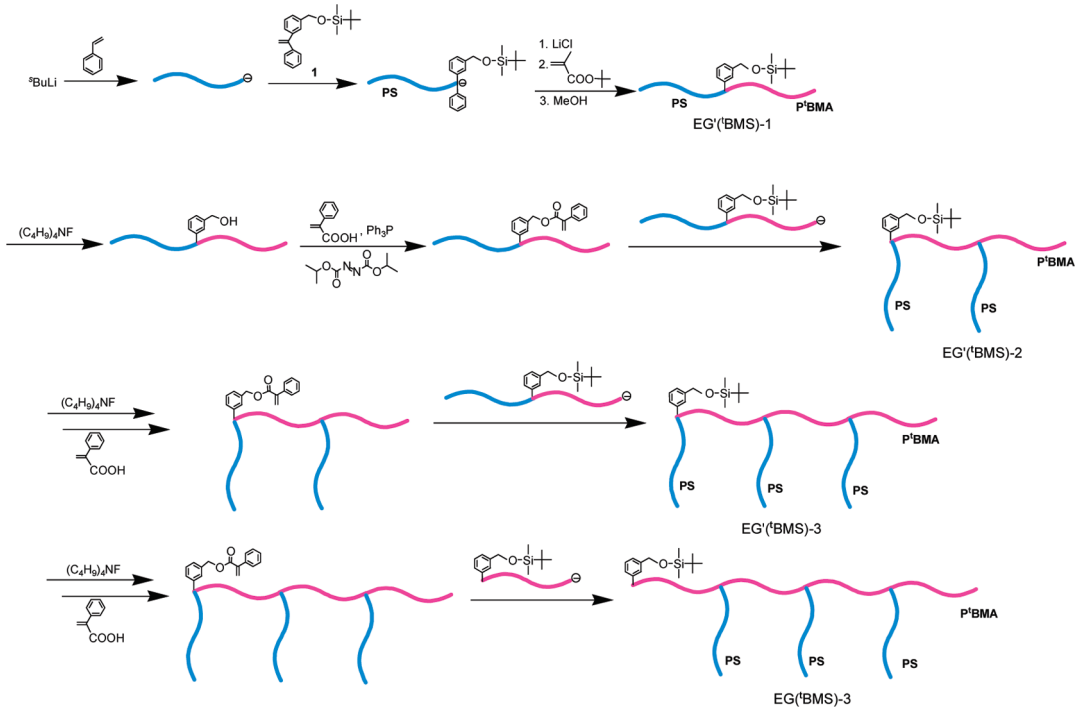
Recently, we have succeed in using α-phenyl acrylate (PA) as a reaction site for the same linking reaction.[16] In fact, the PA reaction site quantitatively reacted with living anionic P^{t}BMA only in a 1:1 addition manner. No further addition of PA took place under the used conditions. Moreover importantly, the PA reaction site could be quantitatively introduced via the SiOMP group under nearly neutral conditions where the *tert*-butyl ester remained completely intact. Thus, the *tert*-butyl ester cleavage of P^{t}BMA can be avoided by replacing the above-used BnBr function with the new PA reaction site. The synthetic outline of the modified methodology is illustrated in Scheme 3.

Similar to Scheme 2 mentioned above, the following three reaction steps are employed in the iterative process: (1) living anionic block copolymerization to prepare a living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA, (2) a transformation reaction of the SiOMP group into PA function via deprotection and subsequent esterification reactions, and (3) a 1:1 addition reaction of the in-chain-PA-functionalized PS-*block*-P^{t}BMA with the living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA to link the two block copolymer chains. The same process involving the three reaction steps can be done several times to construct a series of (P^{t}BMA-*exact graft*-PS)s.

In the first reaction step, the living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA was prepared by living anionic block copolymerization, where styrene, **1**, and ^{t}BMA were sequentially polymerized with *sec*-BuLi in THF at −78 °C. A 5-fold excess of LiCl was added prior to the polymerization of ^{t}BMA to narrow the molecular weight distribution of the produced P^{t}BMA. Throughout the synthesis in this study, the M_n values of not only the PS-*block*-P^{t}BMA but also the other AB block copolymers prepared later are adjusted to be around *ca.* 10 000 g/mol (A(M_n)/B(M_n) = 5000 g/mol/5000 g/mol). The resulting living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA was quenched with degassed methanol and isolated by precipitation in a large amount of methanol. The silyl protective group of the SiOMP group was removed by treatment with $(C_4H_9)_4NF$ and the regenerated benzyl alcohol moiety was reacted with α-phenyl acrylic acid, Ph_3P, and diisopropyl azodicarboxylate (the so-called Mitsunobu reaction) to convert it to the PA function. Quantitative transformation was confirmed by completely shifting the signal at 4.62 ppm assigned to the benzyl CH_2O-Si protons to that at 5.06 ppm corresponding to the benzyl $CH_2O-C(=O)$ protons and by the appearance of the signal at 5.86 for one of the vinyl protons of the PA function. Although one more signal for another vinyl proton at around 6.3 ppm may be present, this is completely overlapped with broad signals of aromatic protons. In addition, the signal assigned to the silyl methyl protons at 0.01 ppm completely disappeared when observed in the same spectrum.

In the second step, an addition reaction was carried out in THF at −40 °C for 24 h between the resulting in-chain-PA-functionalized PS-*block*-P^{t}BMA and a 2-fold excess of the living in-chain-SiOMP-functionalized PS-*block*-P^{t}BMA prepared in a separate experiment. As shown in Figure 2a, the SEC profile of the reaction mixture shows a peak at increased molecular weight corresponding to the target 1:1 addition product. No higher molecular weight peak was produced, indicating that no further addition reaction of the PA group occurred. However, the reaction was not quantitative and was estimated to be 60% in efficiency by comparing the two peak areas (the lower molecular weight peak consists of both of deactivated living diblock copolymer and unreacted PA-functionalized diblock copolymer). The reaction efficiency was not improved by either taking a longer reaction time to 48 h or by raising the reaction temperature to

Scheme 3. Synthesis of Exact Graft Copolymers Composed of PS and P^{t}BMA by a Modified Methodology Using PA Function as a New Reaction Site



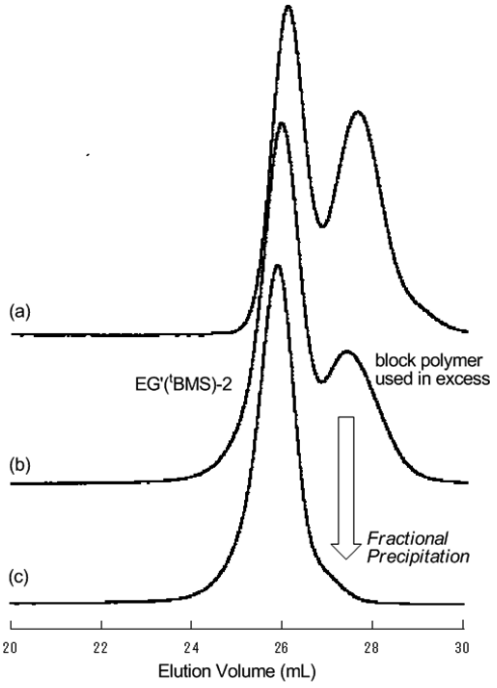


Figure 2. SEC profiles of reaction mixtures: (a) without end-capping with MMA and (b) with end-capping, and EG′(^{t}BMA)-2 after isolation.

−20 °C for 24 h after the first 24 h at −40 °C. The insufficient reaction is most likely due to the steric hindrance of living chain-end of ^{t}BMA. As we previously observed that the 1:1 addition reaction quantitatively occurred between the PA function and living PMMA under the same conditions,[16] a small amount of MMA was added to the living PS-*block*-P^{t}BMA to end-cap the chain-end enolate anion with a few units of MMA. By this end-capping, the addition reaction was found to be complete at −40 °C in 24 h (see Figure 2b). The 1:1 addition product which was isolated by fractional precipitation using a mixture of acetone and methanol, showed a single and narrow molecular weight distribution (M_w/M_n = 1.04) free of the deactivated living block copolymer used in excess (see also Figure 2c). As listed in Table 1, the M_n and composition values observed by SEC-RALLS and ^{1}H NMR are in good agreement with those predicted. Accordingly, all of the analytical results clearly indicate that the three reaction steps satisfactorily proceeded to afford the expected graft copolymer precursor having two PS chains, abbreviated as EG′(^{t}BMS)-2.

Likewise, a graft copolymer precursor having three PS chains (EG′(^{t}BMS)-3) could be synthesized by performing the same iterative process with use of the above-prepared EG′(^{t}BMS)-2 as the starting material. The three reaction steps in the iterative process were traced by ^{1}H NMR and SEC analyses to observe the progress of the reactions. Successful synthesis of a EG′(^{t}BMS)-3 was confirmed by the characterization results listed in Table 1. As the resulting polymer possesses the same SiOMP terminus of the P^{t}BMA backbone chain, it was deprotected and subsequently reacted with α-phenylacrylic acid to convert it to the PA function. Finally, a living P^{t}BMA was linked to the backbone chain to result in an exact graft copolymer composed of a P(^{t}BMA) backbone chain and three PS graft chains (abbreviated as EG(^{t}BMS)-3), as also illustrated in Scheme 3. After the fractionation by SEC, the resulting polymer possesses the observed M_n (34 800 g/mol) and composition (P^{t}BMA/PS = 60/40 (*w*/*w*)) which are in agreement with those (35 100 g/mol and 59/41) predicted.

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Table 1. Synthesis of Exact Graft Copolymer Precursors (EG′(ᵗBMS)-*n* (*n* = 1, 2, and 3)) and a PᵗBMA-*exact graft*-PS (EG(ᵗBMS)-3)

	$M_n \times 10^{-3}$ (g/mol)			M_w/M_n	composition (PᵗBMA/PS, wt/wt)	
code	calcd	SEC[a]	RALLS[b]	SEC[a]	calcd	obsd[c]
EG′(ᵗBMS)-1	11.0	10.8	10.9	1.03	52/48	53/47
EG′(ᵗBMS)-2	20.6	18.1	20.3	1.04	55/45	54/46
EG′(ᵗBMS)-3	30.6	24.5	30.9	1.04	54/46	53/47
EG(ᵗBMS)-3	35.1	27.1	34.8	1.05	60/40	59/41

[a] Estimated by SEC with standard polystyrene samples. [b] Determined by SEC-RALLS equipped with triple detectors. [c] Determined by ^{1}H NMR.

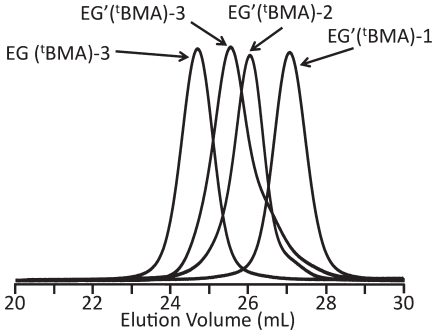


Figure 3. SEC profiles of a series of PᵗBMA-*exact graft*-PS polymers.

A narrow molecular weight distribution was attained. SEC profiles of all PᵗBMA-*exact graft*-PS polymer series are shown in Figure 3.

Thus, a new iterative methodology using PA function as the reaction site instead of the BnBr function works satisfactorily to successfully synthesize the target PᵗBMA-*exact graft*-PS having three PS graft chains. Furthermore, the new methodology is more advantageous than the previous one using the BnBr reaction site because it is applicable to more monomers, especially monomers substituted with acid-labile groups.

Interestingly, EG(ᵗBMS)-3 could be quantitatively converted to a new amphiphilic poly(methacrylic acid)-*exact graft*-PS having three PS graft chains by treatment with Me_3SiCl/LiBr in a mixture of acetonitrile and chloroform.[19] Quantitative conversion was confirmed by FT-IR spectrum, in which *tert*-butyl esters of the PᵗBMA block were completely disappeared. The resulting polymer will be expected to form unique and interesting molecular assemblies by self-organization in aqueous solution or selective solvents.

Synthesis of Exact Graft Copolymers Composed of PFMMA and PS Segments (PFMMA-*exact graft*-PS). By developing the new modified methodology, a new exact graft copolymer composed of a PᵗBMA backbone and three PS graft chains was successfully synthesized. As mentioned before, the new methodology can be more general because various functional methacrylate monomers substituted with acid-labile groups, amenable to living anionic polymerization, are usable. Among such monomers in addition to ᵗBMA, we have herein selected FMMA to synthesize new ferrocene-based exact graft copolymers.

The synthetic outline is exactly the same as that illustrated in Scheme 3 except for the use of FMMA instead of ᵗBMA. A living in-chain-SiOMP-functionalized PS-*block*-PFMMA was synthesized by living anionic block copolymerization, where styrene, **1**, and FMMA were sequentially polymerized with *sec*-BuLi in THF at −78 °C.[20] In this block copolymerization, a 5-fold excess of LiCl was also added prior to the polymerization of FMMA to narrow the molecular weight distribution of the resulting

Table 2. Synthesis of Exact Graft Copolymer Precursors (EG′(FMS)-*n* and EG′(FHS)-*n*, *n* = 1, 2, and 3) and a PFMMA-*exact graft*-PS (EG(FMS)-3)

	$M_n \times 10^{-3}$ (g/mol)			M_w/M_n	composition (w/w)	
code	calcd	SEC[a]	RALLS[b]	SEC[a]	calcd	obsd[c]
EG′(FMS)-1	10.4	6.81	11.9	1.03	47/53	44/56
EG′(FMS)-2	21.6	13.8	21.0	1.03	46/54	44/56
EG′(FMS)-3	31.5	24.4	33.0	1.04	45/55	44/56
EG(FMS)-3	38.3	27.8	39.2	1.04	52/48	50/50
EG′(FHS)-1	8.84	8.11	9.09	1.18	51/49	50/50
EG′(FHS)-2	17.9	9.90	16.2	1.22	50/50	50/50

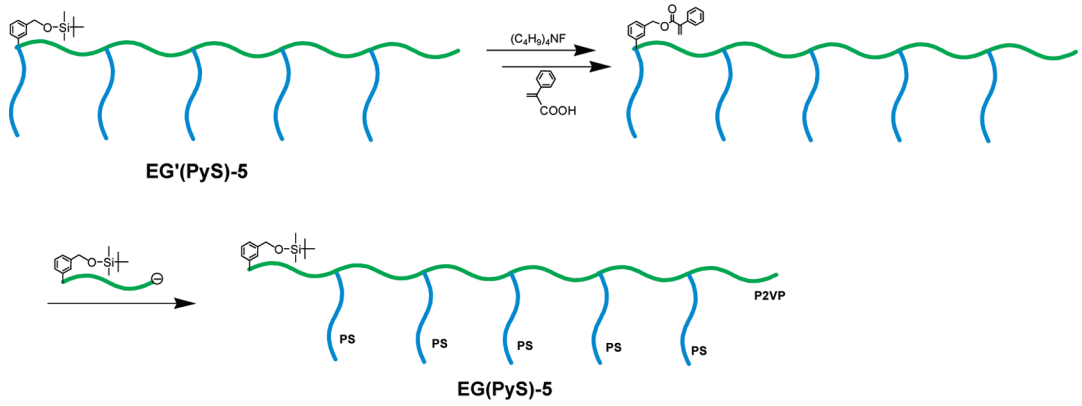
[a] Estimated by SEC with standard polystyrene samples. [b] Determined by SEC-RALLS equipped with triple detectors. [c] Determined by ^{1}H NMR.

PFMMA. The SiOMP group was converted to the PA function in 100% yield without any difficulty under the same conditions as those employed above. In the third reaction step, the living in-chain-SiOMP-functionalized PS-*block*-PFMMA quantitatively underwent a 1:1 addition reaction with the in-chain-PA-functionalized PS-*block*-PFMMA to connect the two block copolymer chains, resulting in an exact graft copolymer precursor having two PS graft chains (EG′(FMS)-2). By performing the same iterative process two times and the subsequent linking reaction with living PFMMA with the resulting graft copolymer precursor having three PS chains (EG′(FMS)-3), a well-defined exact graft copolymer composed of a PFMMA backbone chain and three PS graft chains (EG(FMS)-3) was successfully synthesized.

The characterization results of the intermediate polymers and the final exact graft polymer are summarized in Table 2. Their expected and well-defined structures were demonstrated by good agreement between the observed M_n value and that calculated in each polymer sample. The compositions observed by ^{1}H NMR always agreed well with those calculated. Moreover, all of the polymers possessed sharp monomodal SEC distributions. Thus, the modified methodology is also effective for the synthesis of new ferrocene-based exact graft copolymers. The resulting polymers are attractive functional materials with many potential applications, since such polymers, in addition to their well-defined branched architectures, have many characteristic features originating from ferrocene moieties such as, redox, catalytic, electronic, optoelectronic, photophysical, magnetic, semiconductive, and preceramic properties.[21]

Synthesis of Exact Graft Copolymer Precursor Composed of P(F8H2-MA) and PS Segments (P(F8H2-MA)-*exact graft*-PS). In a similar manner, the synthesis of an exact graft copolymer composed of a poly(2-perfluorooctylethyl methacrylate) (PF_8H_2-MA) backbone chain and two PS graft chains was attempted by developing the same modified methodology using a living

Scheme 4. Synthesis of P2VP-*exact graft*-PS (EG(PyS)-5)



in-chain-SiOMP-functionalized PS-*block*-P(F_8H_2-MA).[22] The use of this living in-chain-functionalized block copolymer is especially attractive from the viewpoint of its solubility, since homopolymers of F_8H_2-MA are insoluble in most organic solvents and precipitate completely at an early stage of anionic polymerization in THF, while (PS-*block*-P(F_8H_2-MA))s having less than 50 wt % of P(F_8H_2-MA) segments, are always soluble in THF even at −78 °C. The insolubility of P(F_8H_2-MA) clearly suggests that homopolymers of F_8H_2-MA can not be directly used as the building blocks in the synthesis of all architectural polymers including exact graft copolymers.

The iterative process involving the three reaction steps was carried out in the same way as that employed above. It was confirmed by ^{1}H NMR and SEC analyses that the preparation of the living in-chain-SiOMP-functionalized PS-*block*-P(F_8H_2-MA), the transformation of the SiOMP group into the PA function, and the 1:1 addition reaction successfully occurred. Unfortunately, the starting block copolymer as well as the resulting graft copolymer precursor having two PS chains (EG′(FHS)-2) was not narrow in molecular weight distribution (M_w/M_n = 1.26) and exhibited a slight tailing, most probably due to the poor solubility. Nevertheless, this result strongly indicates that the synthesis of exact graft copolymers consisting of THF-insoluble P(F_8H_2-MA) segments is possible, but making adjustments to the total molecular weight and composition of the PS-*block*-P(F_8H_2-MA) used as the building block is further optimized.

Synthesis of Exact Graft Copolymers Composed of P2VP and PS Segments (P2VP-*exact graft*-PS). In order to extend the new modified methodology to a more general and versatile synthetic procedure of exact graft copolymers, a series of exact graft copolymers composed of P2VP backbones and PS graft chains were synthesized. For such polymer syntheses, the preparation of a living in-chain-SiOMP-functionalized PS-*block*-P2VP is needed. Since it was previously reported that living P2VP reacted with DPE,[23] several units of **1** of the DPE derivative might be incorporated into the P2VP block during the preparation of a living in-chain-SiOMP-functionalized PS-*block*-P2VP by using an excess amount of **1**. Therefore, a reaction of living P2VP with a 2-fold excess of **1** was examined in THF at −78 °C for 24 h. It was, however, observed that no addition at all of **1** to living P2VP occurred under such conditions. Moreover, it was also confirmed by ^{1}H NMR and SEC-RALLS analyses that a living in-chain-SiOMP-functionalized PS-*block*-P2VP prepared by the living anionic polymerization of styrene and **1**, followed by 2VP, possessed exactly one SiOMP group incorporated in the block copolymer. Accordingly, unlike DPE, **1** could not be reacted with living P2VP.

With use of the living in-chain-SiOMP-functionalized PS-*block*-P2VP thus prepared, the modified methodology has been developed to synthesize a series of (P2VP-*exact graft*-PS)s. The quantitative transformation of the SiOMP group to the PA function also proceeded without difficulty under the same conditions as those previously employed. The addition reaction was carried out in THF at −78 °C for 24 h between the in-chain-PA-functionalized PS-*block*-P2VP and the living in-chain-SiOMP-functionalized PS-*block*-P2VP. In the first iterative process, a 2-fold excess of living block copolymer for the PA function was used and the amount of living polymer was gradually increased with increasing the iteration process in number. A 4-fold excess of living polymer was used at the fourth iteration to force the linking reaction to completion.

The three reaction steps in each iterative process were observed to proceed virtually quantitatively and thereby were repeated four more times. As a result, a series of exact graft copolymer precursors having two, three, four, and five PS graft chains (EG′(PyS)-2, 3, 4, and 5) was successfully synthesized. A living P2VP was further reacted with the PA function of EG′(PyS)-5 to extend the P2VP backbone chain, resulting in the formation of an exact graft copolymer having five PS graft chains (EG(PyS-5)), as shown in Scheme 4. The resulting polymers were isolated in 47−80% yields by fractional precipitation using ethanol and hexane, followed by the fractionation with SEC. The pure polymer samples thus obtained are characterized by ^{1}H NMR and SEC-RALLS and the results summarized in Table 3. All of the polymers possess predictable molecular weights and compositions and narrow monomodal SEC distributions. These results clearly indicate the successful synthesis of the expected and well-defined exact graft polymers. Thus, the proposed methodology also effectively works for the synthesis of P2VP-*exact graft*-PS in addition to P^{t}BMA-*exact graft*-PS and PFMMA-*exact graft*-PS.

Synthetic Attempt of PS-*exact graft*-poly(*N,N*-diethyl acrylamide). We have attempted to synthesize a PS-*exact graft*-poly(*N,N*-diethyl acrylamide) (PAA) by developing a methodology using a living in-chain-SiOMP-functionalized PS-*block*-PAA.[24] The resulting amphiphilic exact graft copolymer is interesting because the backbone PAA chain is water-soluble and shows LCST behavior. The preparation of the living in-chain-SiOMP-functionalized PS-*block*-PAA and the transformation of the SiOMP group into the PA function were successful. However, the addition reaction between the resulting PA-functionalized polymer and the living in-chain-SiOMP-functionalized

Table 3. Synthesis of Exact Graft Copolymer Precursors (EG′(PyS)-*n* (*n* = 1 ∼ 5) and a P2VP-*exact graft*-PS (EG(PyS)-5)

	$M_n \times 10^{-3}$ (g/mol)			M_w/M_n	composition (P2VP/PS, wt/wt)	
code	calcd	SEC[a]	RALLS[b]	SEC[a]	calcd	obs[c]
EG′(PyS)-1	10.7	10.3	10.6	1.03	49/51	50/50
EG′(PyS)-2	20.5	17.1	20.1	1.04	51/49	52/48
EG′(PyS)-3	31.4	25.1	31.1	1.05	52/48	52/48
EG′(PyS)-4	40.9	34.2	39.8	1.05	51/49	51/49
EG′(PyS)-5	49.9	43.1	49.1	1.04	52/48	51/49
EG(PyS)-5	53.6	45.3	5.35	1.06	55/45	56/44

[a] Estimated by SEC with standard polystyrene samples. [b] Determined by SEC-RALLS equipped with triple detectors. [c] Determined by ^{1}H NMR.

PS-*block*-PAA could not proceed in THF at −40 °C for 24 h. Although no occurrence of the addition reaction may be attributed to the instability of the chain-end anion of living PAA or the low reactivity toward the PA function, the synthesis of PAA-*exact graft*-PS is currently still under investigation.

CONCLUSIONS

A variety of exact graft copolymers, such as P^{t}BMA-*exact graft*-PS, PFMMA-*exact graft*-PS, and P2VP-*exact graft*-PS, were successfully synthesized by developing a new modified iterative methodology where living in-chain-SiOMP-functionalized AB diblock copolymers and PA functions are used as the building blocks and new reaction sites. The methodology involves the following three reaction steps in each iterative process: (1) living anionic block copolymerization to prepare an in-chain-SiOMP-functionalized AB diblock copolymer, (2) a transformation of the SiOMP group to the PA function via deprotection and Mitsunobu esterification reactions, and (3) a 1:1 addition reaction between the in-chain-PA-functionalized AB diblock copolymer and the living in-chain-SiOMP-functionalized AB diblock copolymer. The iterative process is performed several times to connect the block copolymer chains, resulting in the formation of exact graft copolymers having three to five PS graft chains. The resulting polymers are all well-defined and precisely controlled with respect to the above-mentioned four parameters which define the structure of a graft copolymer. These four parameters are also individually changed by changing the molecular weights of A and B blocks to be able to synthesize exact graft copolymers with any desired structure. Thus, the new modified methodology herein proposed provides a more general and versatile synthetic procedure, in which changing the transformation reaction and reaction site to the PA function enable the use of more methacrylate monomers substituted with acid-labile groups and 2VP in the iterative methodology.

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REFERENCES

(1) Dreyfus, P.; Quirk, R. P. Graft Copolymers. In *Encyclopedia of Polymer Science and Engineering*; Kroshwitz, J. I., ed.; Wiley-Interscience: New York, 1987, 2nd ed., vol 7, p551.

(2) Cowie, J. M. G. Block and Graft Copolymers. In *Comprehensive Polymer Science*; Allen, G., Bevington, C. J.; Eds. Pergamon: Oxford, U.K., 1989; Vol. 3, p 33.

(3) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization; Principles and Applications*; Marcel Dekker: New York, 1996; p 369.

(4) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747.

(5) Pitsikalis, M.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Adv. Polym. Sci.* **1998**, *135*, 1.

(6) Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.; Mays, J. W. *Prog. Polym. Sci.* **2006**, *31*, 1068.

(7) Properties and morphologies of graft copolymers:(a) Schlegel, R.; Wilkin, D.; Duan, Y.; Weidisch, R.; Heinrich, G.; Uhrig, D.; Mays, J. W.; Iatrou, H.; Hadjichristidis, N. *Polymer.* **2009**, *50*, 6297. (b) Schlegel, R.; Staudinger, U.; Thunga, M.; Weidisch, R.; Heinrich, G.; Uhrig, D.; Mays, J. W.; Iatrou, H.; Hadjichristidis, N. *Europ. Polym. Chem.* **2009**, *45*, 2902. (c) Duan, Y.; Thunga, M.; Schlegel, R.; Schneider, K.; Rettler, E.; Weidisch, R.; Siesler, H. W.; Stamm, M.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **2009**, *42*, 4155. (d) Sun, W.; Yu, F.; He, J.; Zhang, C.; Yang, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46*, 5518. (e) Staudinger, U.; Schlegel, R.; Weidisch, R.; Fritzsche, J.; Klüppel, M.; Heinrich, G.; Mays, J. W.; Uhrig, D.; Hadjichristidis, N. *Eur. Polym. J.* **2008**, *44*, 3790. (f) Flat, J.-J. *Polym. Degrad. Stab.* **2007**, *92*, 2278. (g) Zhu, Y.; Burgaz, E.; Gido, S. P.; Staudinger, U.; Weidisch, R.; Uhrig, D.; Mays, J. W. *Macromolecules* **2006**, *39*, 4428. (h) Mijovic, J.; Sun, M.; Pejanovic, S.; Mays, J. W. *Macromolecules* **2003**, *36*, 7640. (i) Zhu, Y.; Weidisch, R.; Gido, S. P.; Velis, G.; Hadjichristidis, N. *Macromolecules* **2002**, *35*, 5903. (j) Lee, C.; Gido, S. P.; Poulos, Y.; Hadjichristidis, N.; Tan, N. B.; Trevino, S. F.; Mays, J. W. *Polymer* **1998**, *39*, 4631. (k) Se, K.; Yamazaki, H.; Shibamoto, T.; Takano, A.; Fujimoto, T. *Macromolecules* **1997**, *30*, 1570. (l) Lee, C.; Gido, S. P.; Pitsikalis, M.; Mays, J. W.; Tan, N. B.; Trevino, S. F.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 3732. (m) Pochan, D. J.; Gido, S. P.; Pispas, S.; Mays, J. W. *Macromolecules* **1996**, *29*, 5099.

(8) Paraskeva, S.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 931.

(9) Graft copolymers with regularly spaced branch points:(a) Iatrou, H.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 6697. (b) Beyer, F. L.; Gido, S. P.; Büschl, C.; Iatrou, H.; Uhrig, D.; Mays, J. W.; Chang, M. Y.; Garets, B. A.; Balsara, N. P.; Tan, N. B.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 2039. (c) Nakamura, Y.; Wan, Y.; Mays, J. W.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 8323. (d) Uhrig, D.; Mays, J. W. *Macromolecules* **2002**, *35*, 7182.

(10) H- and π-shaped (co)polymers:(a) Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N. *Macromolecules* **1994**, *27*, 6232. (b) Iatrou, H.; Willner, L.; Hadjichristidis, N.; Halperin, A.; Richter, D. *Macromolecules* **1996**, *29*, 581. (c) Gido, S. P.; Lee, C.; Pochan, D. J.; Pispas, S.; Mays, J. W.; Hadjichristidis, N. *Macromolecules* **1996**, *29*, 7022. (d) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1996**, *29*, 7378. (e) Lee, C.; Gido, S. P.; Poulos, Y.; Hadjichristidis, N.; Tan, N. B.; Trevino, S. F.; Mays, J. W. *J. Chem. Phys.* **1997**, *107*, 6460. (f) Hadjichristidis, N.; Xenidou, M.; Iatrou, H.; Pitsikalis, M.; Poulos, Y.; Avgeropoulos, A.; Sioula, S.; Paraskeva, S.; Velis, G.; Lohse, D. J.; Schulz, D. N.; Fetters, L. J.; Wright, P. J.; Mendelson, R. A.; Garcia-Franco, C. A.; Sun, T.; Ruff,

C. J. *Macromolecules* **2000**, *33*, 2424. (g) Haraguchi, N.; Hirao, A. *Macromolecules* **2003**, *36*, 9364. (h) Higashihara, T.; Faust, R.; Inoue, K.; Hirao, A. *Macromolecules* **2008**, *41*, 5616.

(11) Uhrig, D.; Mays, J. W. *Polym. Chem.* **2011**, *2*, 69.

(12) Nikopoulou, A.; Iatrou, H.; Lohse, D.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 2597.

(13) Hirao, A.; Watanabe, T.; Kurokawa, R. *Macromolecules* **2009**, *42*, 3973.

(14) Hirao, A.; Murano, K.; Kurokawa, R.; Watanabe, T.; Sugiyama, K. *Macromolecules* **2009**, *42*, 7820.

(15) Higashihara, T.; Sugiyama, K.; Yoo, H.-S.; Hayashi, M.; Hirao, A. *Macromol. Rapid Commun.* **2010**, *31*, 1031.

(16) Sugiyama, K.; Oie, T.; Abouelmagd, A.; Hirao, A. *Macromolecules* **2010**, *43*, 1403.

(17) Lai, J. C.; Rounsefell, T. D.; Pittman, C. U., Jr. *Macromolecules* **1971**, *4*, 155.

(18) Xie, D.; Tomczak, S.; Hogen-Esch, T. E. *J. Polym. Sci. Part A* **2001**, *39*, 1403.

(19) The conversion P^{t}BMA-*exact graft*-PS (EG(^{t}BMS)-3) to poly(methacrylic acid)-*exact graft*-PS was carried out by treatment with a 5-fold excess of Me_3SiCl/LiBr (1/1, mol/mol) for the *tert*-butyl ester group in acetonitrile and chloroform (1/1, v/v) at 40 °C for 12 h. The polymer was precipitated in water, filtered, and dried in vacuo. The quantitative conversion was confirmed by the FT-IR spectrum. However, the resulting polymer was observed to be insoluble in water, methanol, THF, chloroform, pyridine, and DMF and therefore was not further characterized at the present time.

(20) Hirano, T.; Yoo, H.-S.; Ozama, Y.; Abouelmagd, A.; Sugiyama, K.; Hirao, A. J. *Inorg. Organomet. Polym.* **2010**, *20*, 445.

(21) Abd-El-Aziz, A. S.; Manners, I. *Frontiers in Transition Metal-Containing Polymers*; Wiley-Interscience: Hoboken, NJ, 2007.

(22) Abouelmagd, A.; Sugiyama, K.; Hirao, A. *Macromolecules* **2011**, *44*, 826.

(23) Giebeler, E.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 3815.

(24) Kobayashi, M.; Okuyama, S.; Ishizone, T.; Nakahama, S. *Macromolecules* **1999**, *32*, 6466.