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Precise Synthesis of Miktoarm Star Polymers by Using a New Dual-Functionalized 1,1-Diphenylethylene Derivative in Conjunction with Living Anionic Polymerization System

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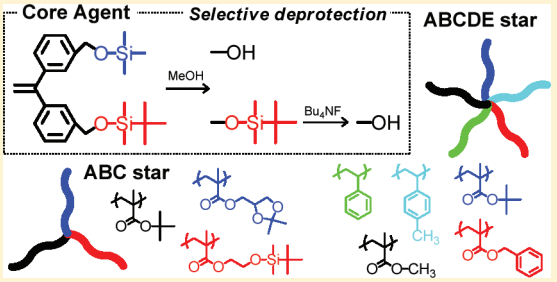
Supporting Information

ABSTRACT: The general utility of a 1,1-diphenylethylene (DPE) derivative substituted with trimethylsilyl- and *tert*-butyldimethylsilyl-protected hydroxyl functionalities, as a new dual-functionalized core agent in conjunction with a living anionic polymerization system, has been demonstrated by the successful synthesis of various well-defined 3-arm ABC and 4-arm ABCD μ-star polymers. Two different protected hydroxyl functionalities were progressively deprotected to generate hydroxyl groups, followed by conversion to α-phenyl acrylate (PA) functions at separate stages, and the PA functions were reacted with appropriate living anionic polymers to result in the above μ-stars. In order to further synthesize μ-star polymers with five or more arms, a new iterative methodology using a functional DPE anion derived from the above DPE derivative has been developed. The reaction system of this methodology is designed in such a way that the PA function used as the reaction site is regenerated after the introduction of an arm segment in each reaction sequence, and this sequence, consisting of "arm introduction and regeneration of the PA reaction site", is repeatable. With this methodology, a series of new well-defined μ-star polymers up to a 5-arm ABCDE type, composed of all different methacrylate-based polymer segments, were successfully synthesized for the first time.



INTRODUCTION

Star-branched polymers have been widely studied for a long time because of synthetic challenges associated with preparing them and because they offer different properties and behavior in solution and bulk from those of the corresponding linear polymers.[1−6] Among the star-branched polymers, asymmetric ones having different arm segments, the so-called mixed arm or miktoarm (from the Greek word $\mu\iota\kappa\tau\acute{o}\zeta$ meaning mixed) star-branched polymers (μ-star polymers),[7−13] have received much attention in recent years because their arm segments are generally phase-separated at the molecular level, followed by self-organizing, to produce new periodical suprastructures and supramolecular assemblies on a nanosize scale which are quite different from those formed by linear block polymers due to their star-branched architectures.[14−27] Such μ-star polymers are expected to play an important role in the very near future as next-generation functional polymers with many potential applications in the fields of nanoscience and nanotechnology.

In order to synthesize well-defined μ-star polymers, the use of living polymerization systems is essential. Among them, the living anionic polymerization is undoubtedly the best system at the present time[28−32] for the synthesis of such well-defined stars possessing precisely controlled and narrowly distributed arm segments, compared to other living/controlled polymerization systems.

In general, μ-star polymers are much more difficult to synthesize than corresponding regular stars having the same number of arm segments, since the synthesis always requires several nearly quantitative reactions for the introduction of a plural number of different arm segments into μ-stars. The currently developed methodologies using the living anionic polymerization system can cover the synthesis of a two-component A_xB_y type. On the other hand, synthetic examples of 3-arm three-component ABC μ-star polymers,[15,33−37] three-component stars with more than 3 arms,[38−42] and 4-arm four-component ABCD μ-stars[43−46] have been very limited so far.

Although the success of the above-mentioned methodologies can be evidenced to a certain extent by possible variation of synthesized μ-star polymers, the reaction site(s) always disappear after the synthesis of target μ-star polymers. None of the methodologies allows for continued further synthesis of μ-star polymers with more arms and compositions. Since 2001, we have developed a novel and versatile methodology, which is based on a new conceptual "iterative approach". In this approach, the reaction system is designed in such a way that the same reaction site is always regenerated after the introduction of an arm segment in each reaction sequence, and this "arm

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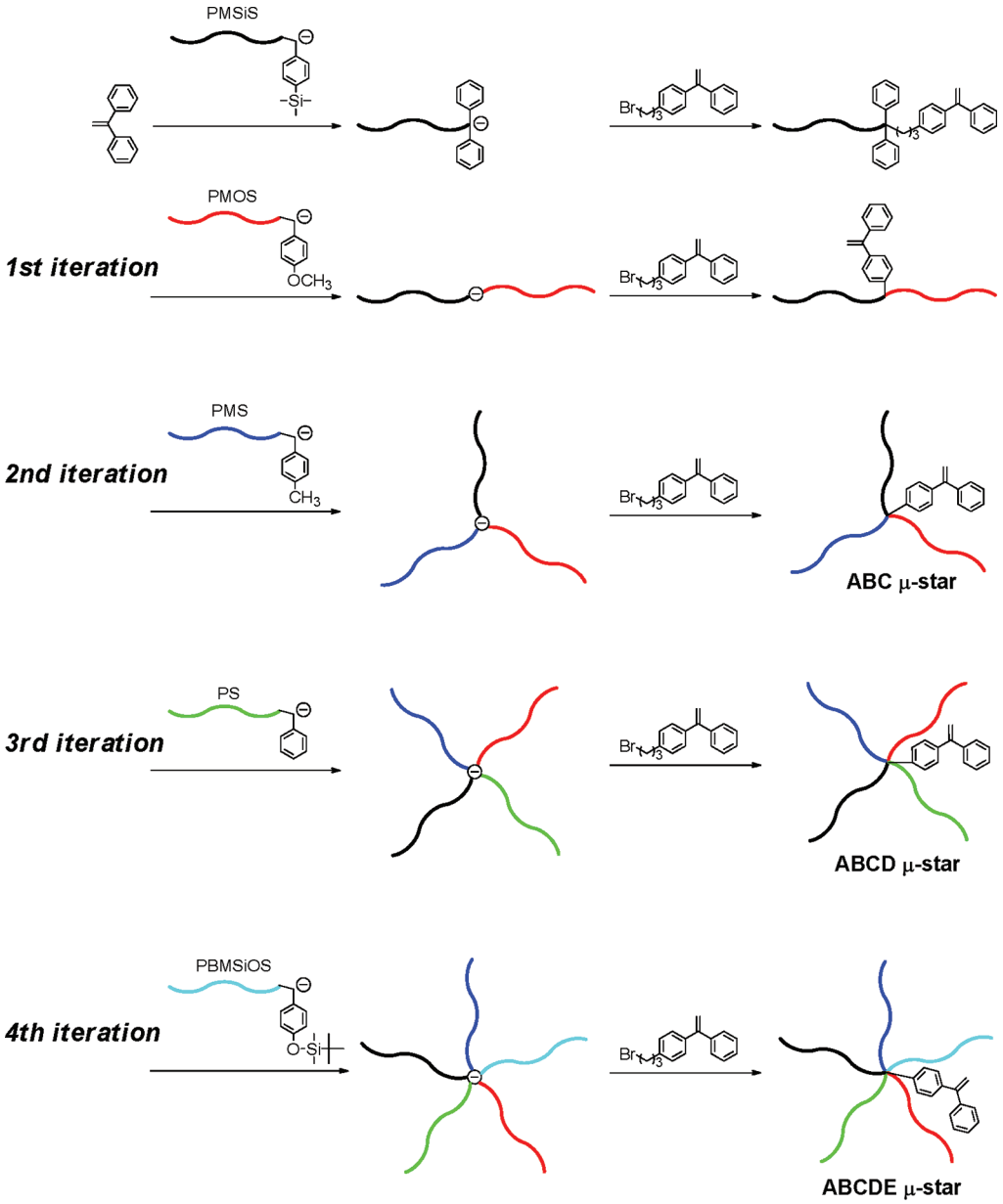
Scheme 1. Iterative Methodology Using DPE Chemistry in Conjunction with Living Anionic Polymerization System



introduction−regeneration of the same reaction site" sequence is repeatable.[11−13,47−49] With this methodology, arm segments can be successively and, in principle, limitlessly introduced by repeating the reaction sequence to afford a series of μ-star polymers with many arms and compositions. Scheme 1 shows a representative iterative methodology using 1,1-diphenylethylene (DPE) chemistry in conjunction with the above living anionic polymerization system.[50] The DPE function is capable of not only reacting with living anionic polymers to link a polymer chain but also of offering a DPE anion for regeneration of the DPE function. The methodology involves only two reaction steps in each reaction sequence: (1) a linking reaction of a living anionic polymer with a chain-DPE-functionalized polymer and (2) regeneration of the DPE function by reacting a specially designed DPE-functionalized agent, 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene (**1**) with the DPE anion produced by the linking reaction. The reaction sequence involving the two reaction steps is repeated several times to successively synthesize a series of μ-star polymers. As can be seen in Scheme 1, the star polymer synthesized in the preceding stage always corresponds to the starting material of the next synthesis.

Synthesis was initiated by the reaction of **1** with a living polymer end-capped with DPE to introduce the DPE function at the chain-end. In the first reaction sequence, another living polymer reacted with the resulting chain-end-DPE-functionalized polymer to link the two polymer chains with the production of a new DPE anion at the linking point. The DPE derivative, **1**, was reacted *in situ* with the DPE anion to regenerate the same DPE function to be used as the next reaction site, resulting in an in-chain-DPE-functionalized AB diblock copolymer. The repetition of the reaction sequence yielded a 3-arm ABC μ-star polymer with the DPE function regenerated at the core. The reaction sequence was repeated two more times to successively synthesize a 4-arm ABCD, followed by a 5-arm ABCDE μ-star polymer. Similar iterative

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methodologies have been further developed to allow access to a wide variety of well-defined μ-star polymers with many arms and components, such as ABC_2, AB_2C_2, $A_2B_2C_2$, $A_3B_3C_3$, AB_2C_4, $ABCD_2$, ABC_2D_2, $AB_2C_4D_8$, $ABCD_2E_2$, and $AB_2C_4D_8E_{16}$ μ-star polymers.[51−61]

Since the living polymer used in the iterative methodology is always required to react with the DPE function in each reaction sequence, only highly reactive living anionic polymers, such as the living polymers of styrene, 1,3-butadiene, isoprene, and their derivatives, can be used. On the other hand, less reactive living polymers of 2-vinylpyridine and alkyl methacrylates, incapable of reacting with the DPE function, are not used. In order to synthesize μ-star polymers consisting of poly(2-vinylpyridine) and/or poly(alkyl methacrylate) segments, the development of a new iterative methodology, in which living anionic polymers of 2-vinylpyridine and alkyl methacrylates are usable, is strongly demanded.

Herein, we report on the general utility of a DPE derivative, 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-(3-trimethylsilyloxymethylphenyl)ethylene (**2**), as a new dual-functionalized core agent in conjunction with the living anionic polymerization system for the synthesis of various well-defined 3-arm ABC and 4-arm ABCD μ-star polymers. Moreover, we also report on the development of a new iterative methodology using a DPE anion derived from **2** for the successive synthesis of a series of μ-star polymers up to a 5-arm ABCDE star composed of all different methacrylate-based polymer segments.

EXPERIMENTAL SECTION

Materials. The reagents (>98% purities) were purchased from Aldrich Japan and used as received unless otherwise stated. Styrene, α-methylstyrene (αMS), 4-methylstyrene (4MS), 4-methoxystyrene (MOS), and 1,1-diphenylethylene (DPE) were washed with 5% NaOH solution and water and dried over $MgSO_4$. After filtration of $MgSO_4$, they were distilled over CaH_2 twice under reduced pressures. Finally, styrene, αMS, 4MS, and MOS were distilled from their Bu_2Mg solutions (ca. 3 mol %) on the vacuum line (10^{-6} Torr). DPE was finally distilled from its 1,1-diphenylhexyllithium (ca. 3 mol %) solution on the vacuum line. 2-Vinylpyridine (2VP) was stirred over KOH overnight. After filtration of KOH, 2VP was finally distilled over fine powder CaH_2 twice on the vacuum line. Methyl methacrylate (MMA), ethyl methacrylate (EMA), *tert*-butyl methacrylate (^{t}BMA), benzyl methacrylate (BnMA), and 2-methoxyethyl methacrylate (MOEMA) were washed with 5% NaOH and water and dried over $MgSO_4$. After filtration of $MgSO_4$, they were finally distilled from their $(C_8H_{17})_3Al$ solutions (ca. 3 mol %) on the vacuum line. 2-*tert*-Butyldimethylsilyloxyethyl methacrylate (Si-HEMA), ferrocenylmethyl methacrylate (PFMMA), and (2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate (acetal-DIMA) were synthesized and purified according to the reported procedures.[62−64] LiCl was dried with stirring at 120 °C for 72 h. All monomers and LiCl were diluted with dry THF and then divided into ampules equipped with break-seals under high-vacuum conditions. α-Phenylacrylic acid was synthesized according to the procedure previously reported.[65] Both 1-(3-hydroxymethylphenyl)-1-phenylethylene and 1,1-bis(3-hydroxymethylphenyl)ethylene were synthesized according to the procedure previously reported.[66]

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 weight 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 40 °C. Three polystyrene (PS) gel columns (pore size (bead size)) were used: 650 Å (9 μm), 200 Å (5 μm), 75 Å (5 μm). The relative molecular weights were determined by SEC with RI detection using standard polystyrene 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, diblock copolymers, and star-branched polymers.

Synthesis of 1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-(3-trimethylsilyloxymethylphenyl)ethylene (2). To the solution of 1,1-bis(3-hydroxymethylphenyl)ethylene (7.15 g, 29.8 mmol) and imidazole (2.03 g, 29.8 mmol) dissolved in dry DMF (40 mL) was added *tert*-butyldimethylsilyl chloride (4.49 g, 29.8 mmol) in dry DMF (20 mL), and the mixture was stirred at 25 °C for 4 h. The mixture was quenched with saturated aqueous $NaHCO_3$ (50 mL), extracted with diethyl ether, washed with water, and dried over anhydrous $MgSO_4$. After the removal of solvent under reduced pressure, silica gel column chromatography treated with triethylamine (hexane/dichloromethane = 5/1 (v/v)) afforded 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-(3-hydroxymethylphenyl)ethylene in 20% yield (3.61 g, 10.2 mmol). 1-(3-*tert*-Butyldimethylsilyloxymethylphenyl)-1-(3-hydroxymethylphenyl)ethylene thus prepared (3.59 g, 10.1 mmol) was mixed with hexamethyldisilazane (3.25 g, 20.1 mmol) in nitromethane (25 mL), and the mixture was allowed to react at 25 °C for 20 min under nitrogen. Removal of all volatile compounds by vacuum pump (10^{-1} Torr), followed by the high-vacuum conditions (10^{-6} Torr), yielded 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-(3-trimethylsilyloxymethylphenyl)ethylene (**2**) (4.31 g, 10.1 mmol, ~100%). In order to remove trace amounts of impurities that can react with anionic species, **2** was finally purified under a high-vacuum line by carefully adding *sec*-BuLi in heptane (0.05 M) until the color change from colorless to faint yellow: 300 MHz ^{1}H NMR ($CDCl_3$) δ = 7.30−7.19 (m, 8H, Ar), 5.45, 5.44 (s, 2H, =CH_2), 4.73, 4.68 (s, 4H, −CH_2−O−), 0.91 (s, 9H, −C−(CH_3)$_3$), 0.14 (s, 9H, −Si−(CH_3)$_3$), 0.08 (s, 6H, −Si−(CH_3)$_2$). 75 MHz ^{13}C NMR ($CDCl_3$) δ = 141.6, 141.5, 141.1, 140.9, 128.3, 128.2, 127.3, 127.0, 126.6, 126.1, 126.0, 125.5 (Ar), 150.2 (C=CH_2), 114.3 (C=CH_2), 65.0, 64.7 (−CH_2−O−), 26.3 (−C−(CH_3)$_3$), 18.5 (−C−(CH_3)$_3$), −0.2 (−Si−(CH_3)$_3$), −5.1 (−Si−(CH_3)$_2$).

General Procedure of Postpolymerization, Model Linking Reaction, and μ-Star Polymer Syntheses. Except for deprotection and the Mitsunobu esterification reaction, all of the polymerizations and linking reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed handmade glass reactors equipped with break-seals. The reactor was sealed off from the vacuum line and prewashed with a red colored 1,1-diphenylhexyllithium (ca. 0.05 M) in heptane solution prior to the polymerization and linking reaction. All operations were performed according to the usual high-vacuum technique with break-seals.

Stability Evaluation of Living PMMA by Postpolymerization. A typical procedure is as follows: MMA (5.90 mmol) in THF solution (4.80 mL) was first polymerized with the initiator prepared from *sec*-BuLi (0.0797 mmol) and DPE (0.160 mmol) in the presence of LiCl (0.430 mmol) in THF solution (3.45 mL) at −78 °C for 20 min. Then, the polymerization mixture was allowed to stand at −40 °C for 2 h. It was again cooled to −78 °C, and the postpolymerization was subsequently carried out at −78 °C for 30 min by adding MMA (5.78 mmol) in THF solution (4.70 mL) precooled at −78 °C. The polymerization was quenched with degassed methanol. Polymers were recovered by the precipitation in hexane and analyzed by SEC and RALLS. The postpolymerization of ^{t}BMA, BnMA, or Si-HEMA was carried out in similar manners.

Model Linking Reaction of Living PMMA with Chain-End-PA-Functionalized PS. A typical procedure is as follows: A chain-end-PA-functionalized PS was prepared by the procedure reported in the Supporting Information. MMA (5.21 mmol) in THF solution (5.18 mL) was polymerized at −78 °C for 20 min with the initiator prepared from *sec*-BuLi (0.0444 mmol) and DPE (0.0683 mmol) in the presence of LiCl (0.149 mmol) in THF solution (3.42 mL). Then, the chain-end-PA-functionalized PS ($M_{n,SEC}$ = 10.7 kg/mol, 0.0154 mmol for the PA function) in THF solution (2.07 mL) was added to the living PMMA solution, and the mixture was allowed to react at

−78 °C for 20 h. After quenching with degassed methanol, the polymer mixture was precipitated in hexane and analyzed by SEC and RALLS. The reaction efficiency was estimated by comparing SEC peak areas corresponding to those of the linked polymer, deactivated PMMA, and unreacted PS. Similarly, the linking reaction of living PMMA or P^{t}BMA with the same chain-end-PA-functionalized PS was carried out under various conditions listed in Table 2. The syntheses of chain-end-PA-functionalized PS and other chain-end-functionalized (PS)s are reported in the Supporting Information.

Synthesis of 3-Arm AA′A″ Star PMMA and 3-Arm ABC μ-Star Polymers. MMA (12.3 mmol) in THF solution (11.6 mL) was polymerized at −78 °C for 20 min with the initiator prepared from oligo(α-methylstyryl)lithium (0.103 mmol) (*sec*-BuLi (0.103 mmol) and α-methylstyrene (0.433 mmol)) and **2** (0.153 mmol) in the presence of LiCl (0.449 mmol) in THF solution (9.42 mL). The polymerization was terminated with degassed methanol, and the polymer was precipitated in methanol containing a few drops of acetic acid. It was reprecipitated from THF to methanol and freeze-dried from its absolute benzene solution. In the precipitation step, the TMS functionality of **2** was selectively deprotected to regenerate the hydroxyl group. Thus, a chain-end-(hydroxyl and TBDMS-protected hydroxyl)-functionalized PMMA was obtained in 98% yield (1.26 g) and characterized by SEC, RALLS, and ^{1}H NMR. M_n(RALLS) = 13.6 kg/mol, M_w/M_n = 1.05 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.66 (s, Ar−CH_2−OSi), 4.62 (s, Ar−CH_2−OH), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 0.05 (s, Si−(CH_3)$_2$).

Under an atmosphere of nitrogen, the chain-end-functionalized PMMA (0.0926 mmol for the hydroxyl functionality) dissolved in dry THF (15 mL) was mixed with PPh_3 (5.76 mmol), α-phenylacrylic acid (5.76 mmol), and diisopropyl azodicarboxylate (DIAD) (5.74 mmol) at 0 °C. The reaction mixture was allowed to react at 25 °C for 16 h and poured into methanol to precipitate the polymer. The polymer was purified by reprecipitation twice from THF solution to methanol and freeze-dried from its absolute benzene solution for 24 h. The polymer was obtained in 89% yield (1.12 g). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 6.31 and 5.87 (s, C=CH_2), 5.19 (s, Ar−CH_2−OCO), 4.66 (s, Ar−CH_2−Si), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 0.05 (s, Si−(CH_3)$_2$).

MMA (10.4 mmol) was polymerized at −78 °C for 20 min with the initiator prepared from *sec*-BuLi (0.104 mmol) and DPE (0.135 mmol) in the presence of LiCl (0.339 mmol) in THF solution (17.2 mL). The resulting living PMMA (0.104 mmol) was *in situ* reacted with the above chain-end-(PA and TBDMS-protected hydroxyl)-functionalized PMMA (0.0298 mmol for PA functionality) in THF solution (5.47 mL), precooled at −78 °C. The reaction mixture was allowed to further react at −40 °C for 20 h. The reaction was quenched with degassed methanol, and polymers were precipitated in hexane. The target in-chain-(TBDMS-protected hydroxyl)-functionalized PMMA was isolated in 80% yield by fractional precipitation using benzene/methanol (1/5 (v/v)) and reprecipitated in methanol and freeze-dried from its absolute benzene solution for 24 h (0.579 g, 74%). M_n(RALLS) = 26.2 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.96 (s, Ar−CH_2−OCO−), 4.66 (s, Ar−CH_2−OSi), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 0.05 (s, Si−(CH_3)$_2$).

Under an atmosphere of nitrogen, the resulting in-chain-(TBDMS-protected hydroxyl)-functionalized PMMA (0.0221 mmol), dissolved in THF (8.0 mL), was mixed with $(C_4H_9)_4NF$ (0.663 mmol) in THF solution (0.663 mL) at −10 °C. The reaction mixture was allowed to stir at −10 °C for 10 h and then poured into a large amount of methanol to precipitate the polymer. The polymer was purified by reprecipitation from THF to methanol and freeze-dried from its absolute benzene solution (0.556 g, 96%). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.96 (s, Ar−CH_2−OCO−), 4.62 (s, Ar−CH_2−OH), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone).

The resulting in-chain-hydroxyl-functionalized PMMA (0.0212 mmol for the hydroxyl group) was esterified with α-phenylacrylic acid in the same manner as that mentioned above. The polymer was purified by the reprecipitation three times from THF solution to methanol and freeze-dried from its absolute benzene solution for 24 h (0.500 g, 90%). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, Ar), 6.31 (s, C=CH_2), 5.87 (s, C=CH_2), 5.19 (s, Ar−CH_2−OCO−CH(C_6H_5)=CH_2), 4.96 (s, Ar−CH_2−OCO−CH(C_6H_5)−CH_2−), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone).

Finally, the in-chain-PA-functionalized PMMA (0.0152 mmol for the PA function) thus prepared was reacted at −40 °C for 20 h with living PMMA (0.0511 mmol, M_n(RALLS) = 10.4 kg/mol) prepared in the same manner mentioned above. The target 3-arm AA′A″ star-branched PMMA was isolated in 80% yield by fractional precipitation using benzene/methanol (1/5, v/v) (0.622 g). M_n(RALLS) = 36.8 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, Ar), 4.96 (s, Ar−CH_2-O−), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone).

The 3-arm ABC μ-star polymers were synthesized by using the similar procedures mentioned above, and details are reported in the Supporting Information.

Synthesis of 4-Arm ABCD μ-Star Polymers. The synthesis of 4-arm ABCD μ-star polymers was also carried out by using the above-mentioned similar procedures except for the use of in-chain-functionalized PS-*block*-PMMA, and details are reported in the Supporting Information.

Successive Synthesis of μ-Star Polymers by a New Iterative Methodology. A chain-end-(TMS- and TBDMS-protected hydroxyl)-functionalized-PMMA was newly prepared in the same manner as that mentioned above and used as the starting material in the methodology.

The First Iterative Process. The TMS-protected hydroxyl functionality of the above-mentioned starting polymer was selectively deprotected in methanol containing a few drops of acetic acid, and the generated hydroxyl group was converted to the PA function, resulting in a chain-end-(PA and TBDMS-protected hydroxyl)-functionalized PMMA in 92% yield. M_n(RALLS) = 13.2 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.66 (s, Ar−CH_2−OSi), 4.62 (s, Ar−CH_2−OH), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 0.05 (s, Si−(CH_3)$_2$).

Living PEMA was prepared at −78 °C for 30 min by the polymerization of EMA (16.3 mmol) in THF solution (14.5 mL) with the initiator prepared from *sec*-BuLi (0.183 mmol) and DPE (0.229 mmol) in the presence of LiCl (0.585 mmol) in THF solution (11.1 mL) and *in situ* reacted with the above chain-end-(PA and TBDMS-protected hydroxyl)-functionalized PMMA (0.0592 mmol for the PA function) in THF solution (10.5 mL) at −78 °C. The reaction mixture was allowed to further react at −40 °C for 20 h. After the usual work-up, an in-chain-(TBDMS-protected hydroxyl)-functionalized PMMA-*b*-PEMA was isolated in 68% yield by SEC fractionation (0.930 g). M_n(RALLS) = 23.1 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.96 (s, Ar−CH_2−OCO−), 4.66 (s, Ar−CH_2−OSi), 4.05 (s, −O−CH_2−CH_3), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 0.05 (s, Si−(CH_3)$_2$).

The TBDMS-protected hydroxyl functionality was deprotected with $(C_4H_9)_4NF$ at −10 °C for 10 h, and the generated hydroxyl group was converted to the PA function. The functional DPE anion was prepared from **2** (0.113 mmol) and oligo(α-methylstyryl)lithium (0.0754 mmol) (*sec*-BuLi (0.0754 mmol) and α-methylstyrene (0.263 mmol)) in THF solution (5.60 mL) at −78 °C for 30 min and *in situ* reacted with the above in-chain-PA-functionalized PMMA-*b*-PEMA (0.0565 mmol for the PA function) at −78 °C for 10 h. The reaction was quenched with degassed methanol containing a few drops of acetic acid. The polymer, once precipitated in a mixture of methanol and water (5/1, v/v), was reprecipitated from its THF solution to a mixture of methanol and water (5/1, v/v) and freeze-dried twice from its absolute benzene solution. An in-chain-(hydroxyl and TBDMS-protected hydroxyl)-functionalized PMMA-*b*-PEMA was obtained in 93% yield (0.727 g). M_n(RALLS) = 23.0 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.96 (s, Ar−CH_2−OCO−), 4.66 (s, Ar−CH_2−OSi), 4.62 (s, Ar−CH_2−OH), 4.05 (s, −O−CH_2−CH_3), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 0.05 (s, Si−(CH_3)$_2$).

The Second Iterative Process. The hydroxyl group of the above in-chain-functionalized PMMA-*b*-PEMA was converted to the PA function in the same manner as that mentioned above. Thus, an in-chain-(PA and TBDMS-protected hydroxyl)-functionalized PMMA-*b*-PEMA was prepared in 92% yield.

Living P^{t}BMA (0.103 mmol, M_n(RALLS) = 10.7 kg/mol) was reacted with the in-chain-(PA and TBDMS-protected hydroxyl)-functionalized PMMA-*b*-PEMA (0.0299 mmol for the PA function) at −25 °C for 20 h to yield a core-(TBDMS-protected hydroxyl)-functionalized 3-arm ABC μ-star polymer, composed of PMMA, PEMA, and P^{t}BMA. The polymer was isolated in 87% yield by SEC fractionation (0.881 g). M_n(RALLS) = 33.8 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.96 (s, Ar−CH_2−OCO−), 4.66 (s, Ar−CH_2−OSi), 4.05 (s, −O−CH_2−CH_3), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 1.44 (s, −C−$(CH_3)_3$), 0.05 (s, Si−$(CH_3)_2$).

In the resulting star, the TBDMS-protected hydroxyl functionality was deprotected to generate the hydroxyl group, followed by conversion to the PA function, and the PA function thus regenerated was reacted with the DPE anion prepared in the same manner mentioned above to introduce both the TMS- and the TBDMS-protected hydroxyl functionalities.

The Third Iterative Process. The TMS-protected functionality of the above core-functionalized μ-star polymer was selectively deprotected in methanol containing a few drops of acetic acid, and the generated hydroxyl group was converted to the PA function. Thus, a core-(PA and TBDMS-protected hydroxyl)-functionalized 3-arm ABC μ-star polymer was obtained in 96% yield.

Living PBnMA was prepared at −78 °C for 1 h by the polymerization of BnMA (4.12 mmol) with the initiator prepared from *sec*-BuLi (0.0788 mmol) and DPE (0.108 mmol) in the presence of LiCl (0.272 mmol) and *in situ* reacted with the core-(PA and TBDMS-protected hydroxyl)-functionalized ABC μ-star polymer (0.0213 mmol for the PA function) at −78 °C. The reaction mixture was then allowed to react at −40 °C for 20 h. After the usual work-up, a core-(TBDMS-protected hydroxyl)-functionalized 4-arm ABCD μ-star, composed of PMMA, PEMA, P^{t}BMA, and PBnMA, was isolated in 85% yield by SEC fractionation (0.779 g). M_n(RALLS) = 43.0 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.88 (s, −CH_2−Ph) 4.66 (s, Ar−CH_2−OSi), 4.05 (s, −O−CH_2−CH_3), 3.59 (s, −O−CH_3), 2.07−0.70 (broad, backbone), 1.44 (s, −C−$(CH_3)_3$), 0.05 (s, Si−$(CH_3)_2$).

In the resulting star, the TBDMS-protected hydroxyl functionality was deprotected to generate the hydroxyl group, followed by conversion to the PA function, and the PA function thus regenerated was reacted with the DPE anion prepared in the same manner mentioned above to introduce both the TMS- and the TBDMS-protected hydroxyl functionalities.

The Fourth Iterative Process. The TMS-protected functionality of the above core-functionalized μ-star polymer was selectively deprotected in methanol containing a few drops of acetic acid, and the generated hydroxyl group was converted to the PA function. Thus, a core-(PA and TBDMS-protected hydroxyl)-functionalized 4-arm ABCD μ-star polymer was obtained in 87% yield.

Living PMOEMA was prepared at −78 °C for 2 h by the polymerization of MOEMA (4.95 mmol) with the initiator prepared from *sec*-BuLi (0.0502 mmol) and DPE (0.0864 mmol) in the presence of LiCl (0.183 mmol) and *in situ* reacted with the core-(PA and TBDMS-protected hydroxyl)-functionalized ABCD μ-star polymer (0.0127 mmol for the PA function) at −78 °C. Then, the reaction mixture was allowed to react with at −40 °C for 20 h. After the usual work-up, a 5-arm ABCDE μ-star polymer, composed of PMMA, PEMA, P^{t}BMA, PBnMA, and PMOEMA, was isolated in 54% yield by fractional precipitation using methanol/water (5/1, v/v) (0.353 g). M_n(RALLS) = 51.5 kg/mol, M_w/M_n = 1.03 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.24−6.93 (m, aromatic), 4.88 (s, −CH_2−Ph) 4.66 (s, Ar−CH_2−OSi), 4.24−3.96 (m, −O−CH_2−CH_3, −O−CH_2−CH_2−O−), 3.59 (s, COO−CH_3), 3.38 (s, −CH_2−CH_2−O−CH_3) 2.07−0.70 (broad, backbone), 1.44 (s, −C−$(CH_3)_3$), 0.05 (s, Si−$(CH_3)_2$).

The successive synthesis of μ-stars by using living P4MS chain-end-functionalized with **2** is reported in the Supporting Information.

RESULTS AND DISCUSSION

Stability of Living Poly(methyl methacrylate) (PMMA) and Poly(*tert*-butyl methacrylate) (P^{t}BMA). In this study, we focus on the synthesis of new μ-star polymers mainly composed of methacrylate-based polymer segments. However, there is so far little information on the stability of living anionic polymers of MMA and other alkyl methacrylate monomers, although it is extremely important in the synthesis of such star-branched polymers. For this reason, living polymers of both MMA and ^{t}BMA were selected as representative examples, and the stability was examined by postpolymerization, prior to star polymer synthesis. Stability is evaluated by comparing two SEC peak areas of the first polymer with the postpolymer and by comparing the observed M_n value of the postpolymer with that calculated from the feed ratio. For example, living MMA was prepared by the polymerization with the initiator prepared from *sec*-BuLi and DPE in the presence of a 3-fold excess of LiCl in THF at −78 °C for 20 min and then allowed to stand at −40 °C for 2 h. The living PMMA was again cooled to −78 °C, and the postpolymerization was carried out at −78 °C for 30 min by adding a second MMA to the mixture. It has already been ascertained that living PMMA is obtained within 10 min and completely stable at −78 °C for 1 h. The SEC profile, as shown in Figure 1, clearly exhibits two distinct peaks, which

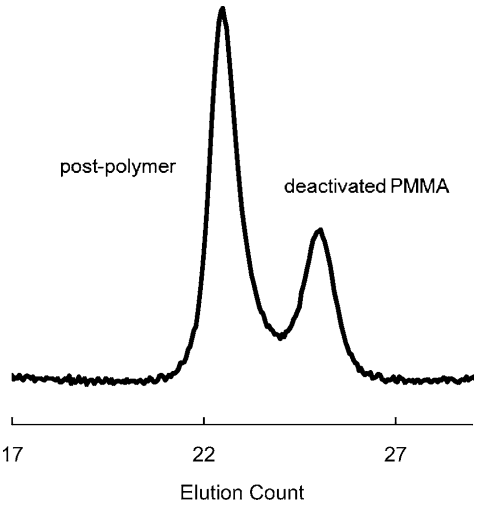

Figure 1. SEC profiles of deactivated PMMA and postpolymer obtained by the postpolymerization.

correspond to those for PMMA deactivated after the first polymerization and the postpolymer. The stability of living PMMA at −40 °C for 2 h is calculated to be 41% by comparing the two peak areas. It is also calculated to be 38% by comparing the M_n value (26.7 kg/mol) of the postpolymer with the predictable value (14.9 kg/mol) by assuming that the first living PMMA is completely stable. An average value ((41 + 38)/2 = 40%) was adopted as the stability under the condition at −40 °C for 2 h. Additional results obtained under various conditions are summarized in Table 1.

Living PMMA was stable at −78 °C for 1 h, but slowly deactivated with time. It survived 90% and 85% after 10 and 20 h, respectively. It became unstable by raising the temperature to −40 °C and only 40% and 27% of the original chain-end anion

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Table 1. Stability of Living PMMA, P^{t}BMA, PBnMA, and P(Si-HEMA) in THF

living polymer	temp (°C)	time (h)	stability (%)
PMMA	−78	10	90
	−78	20	85
	−40	2	40
	−40	5	27
	−20	2	0
P^{t}BMA	−78	20	100
	−40	5	88
	−25	2	20
	−25	5	0
PBnMA	−78	20	90
	−40	2	50
P(Si-HEMA)	−78	20	70
	−40	2	60

survived after 2 and 5 h, respectively. The chain-end anion was completely deactivated at −20 °C after 2 h. In contrast, living P^{t}BMA appeared to be more stable.[67] For instance, it was completely stable at −78 °C even after 20 h. Of the original anion, 88% remained active at −40 °C after 5 h. However, living P^{t}BMA was not stable at −25 °C (only 20% active after 2 h) and completely deactivated after 5 h.

It was also observed that chain-end anions of living P(Si-HEMA) and PBnMA survived 70% and 90% at −78 °C after 20 h. As expected, their activities decreased 60% and 50%, respectively, at −40 °C after 2 h. Thus, they are less stable in activity than living P^{t}BMA, but similar to living PMMA. Although the stability of living polymers obtained from other methacrylate monomers used in this study have not been examined yet, we estimate from the results on the stability of living P(Si-HEMA) and PBnMA that their living polymers may be similar in stability to living PMMA because their ester moieties are primary types like the case of MMA.

Model Linking Reaction of Either Living PMMA or P^{t}BMA with Chain-End-PA-Functionalized PS. As already reported in our previous papers,[38,68−72] the PA function introduced at the polymer chain-end was quantitatively reacted with highly reactive living polymers of styrene and 2VP to link the polymer chains to each other at −78 °C within a few hours. A 1.5-fold excess of each living polymer for the PA function was enough to complete the reaction. As shown in Scheme 2, this reaction is not a coupling reaction, but a 1:1 addition reaction and no further addition of the PA function occurred at −78 °C under the conditions using excess amounts of living polymers. A new enolate anion was produced from the PA function after the linking reaction but could not be used in the further linking reaction or polymerization due to its low reactivity and stability.

Unlike the reaction of the PA function with living PS or P2VP, living PMMA reacted very sluggishly with the PA function at −78 °C and was far from complete even after 20 h. The reaction proceeded quantitatively at −40 °C for 20 h by using a 3-fold excess of living PMMA for the PA function. It should once again be mentioned that neither polymerization nor even oligomerization of the PA function occurred under such conditions.

In this section, we searched for more optimized reaction conditions and other new reaction sites capable of linking with living PMMA. A model reaction was carried out between living PMMA (M_n = ca. 5.00−10.0 kg/mol) and chain-end-PA-functionalized PS (M_n = 10.7 kg/mol) in THF under various conditions, and the efficiency under each reaction condition is listed in Table 2. As mentioned above, the reaction was not

Table 2. Model Linking Reaction between Chain-End-PA-Functionalized PS and Living PMMA or P^{t}BMA in THF

living polymer	temp (°C)	[PΘ]/[PA] (mol/mol)	time (h)	reaction efficiency (%)
PMMA	−78	3.0	20	35
	−40	3.0	10	100
	−40	2.0	10	60
	−20	2.2	10	65
P^{t}BMA	−78	2.6	20	48
	−40	2.8	10	70
	−25	3.0	10	100

[a]Equivalent of living polymer for PA function.

complete at −78 °C. The reaction efficiency was only 35% after 20 h using a 3-fold excess of living PMMA. It gradually increased for longer reaction times but was far from complete (∼50%) even after 72 h. A quantitative reaction was achieved by raising the reaction temperature to −40 °C and using a 3-fold of living PMMA for 10 h. The reaction efficiency decreased to 60% by decreasing the amount of living PMMA to a 2-fold excess. Because of the instability of living PMMA at −40 °C listed in Table 1 and the sluggish reaction rate, a 3-fold of living PMMA may be required to complete the reaction. The reaction efficiency at −20 °C was observed to be 65% using a 2.2-fold excess of living PMMA. This result was surprising, taking into consideration that the living PMMA was completely deactivated at −20 °C within 2 h (see Table 1).

Next, the linking reaction of living P^{t}BMA (M_n = ca. 5.00−10.0 kg/mol) with chain-end-PA-functionalized PS (M_n = 10.7 g/mol) was also performed under various conditions, and those results are also summarized in Table 2. Again, the reaction was sluggish at −78 °C and incomplete even after 20 h. As expected, the reaction efficiency was increased by raising the reaction temperature to −40 °C. However, the efficiencies obtained by several repeated reactions were around 70% with the use of a 2.8-fold excess of living P^{t}BMA. The reaction was observed to quantitatively proceed at −25 °C for 10 h with a 3-fold excess of living P^{t}BMA. The reaction seemed to be complete within 1 h, as estimated from the stability at −25 °C listed in Table 1. Based on these results, reaction conditions at −40 and −25 °C were employed for living PMMA and P^{t}BMA, respectively. In each case, a 3-fold excess of living polymer was used and the reaction time was set at 20 h for convenience of

Scheme 2. 1:1 Addition Reaction of Living Anionic Polymer with Chain-End-PA-Functionalized Polymer

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experimental operation. In the linking reaction of the PA terminus with a living polymer of another methacrylate monomer, the former condition at −40 °C for 20 h was first used. If the reaction was not complete under such a condition, the latter condition at −25 °C for 20 h necessary for completion with the use of living P^{t}BMA was employed. All of the linking reactions carried out in this study were actually observed to be complete at −40 °C for 20 h using a 3-fold excess of living polymer for the PA function.

In order to explore other agents effective in the linking reaction, the following chain-end-functionalized (PS)s (M_n = 10.7 kg/mol), as shown in Figure 2, were newly prepared and

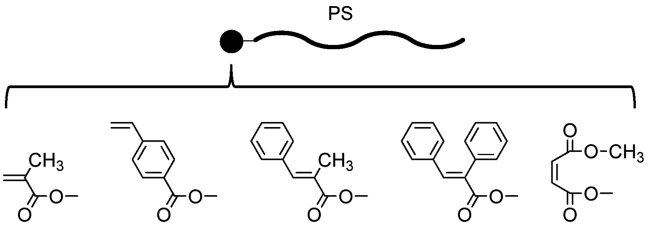


Figure 2. Chain-end-functionalized (PS)s with various reaction sites.

used in the linking reaction with living PMMA. The results are summarized in Table 3. Living PMMA efficiently reacted with a chain-end-(methacrylate)-functionalized PS at −40 °C for 20 h (77% efficiency). Unfortunately, a further addition reaction of the methacrylate terminus with the enolate anion produced after the reaction occurred to some extent. The efficiency was 49% in the linking reaction between a chain-end-(4-vinylbenzoate)-functionalized PS and a 2.2-fold excess of living PMMA. It was not improved by using a 3-fold excess of living PMMA. No reaction occurred between living PMMA or with either of the α, β-disubstituted acrylate termini at −40 °C, possibly due to steric hindrance.

Table 3. Model Linking Reaction between Living PMMA and Chain-End-Functionalized PS with Various Reaction Sites in THF at −40 °C for 20 h

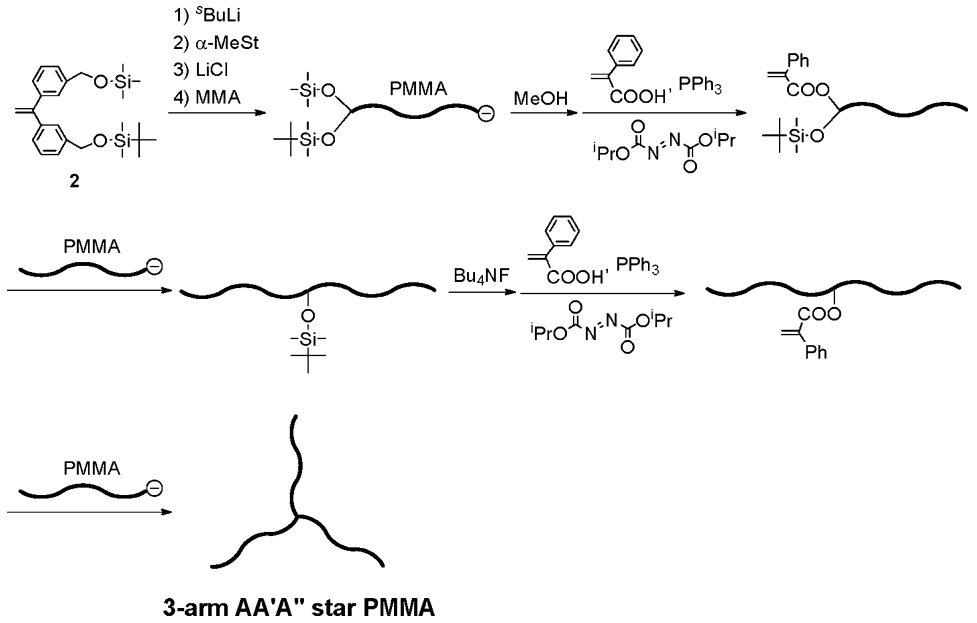
chain-end-functionalized PS reaction site[a]	reaction efficiency (%)
methacrylate	77
4-vinylbenzoate	49
α-methylcinnamate	0
α-phenylcinnamate	0
methyl maleate	100

[a][Living PMMA]/[reaction site] = 2.2−3.0.

A methyl maleate terminus quantitatively reacted with living PMMA (a 2.2-fold excess) at −40 °C for 20 h. On the other hand, the linking reaction of the chain-end-(methyl maleate)-functionalized PS with either the living PS end-capped with DPE or living P2VP was always stopped at around 20−30% yield at −78 °C for 10 h. This is probably due to proton abstraction from the maleate vinylene group by living polymer anions. Among the reaction sites examined, the PA function was eventually the best reaction site and, therefore, used in the linking reaction to synthesize star-branched polymers throughout this study.

General Utility of 2 in μ-Star Polymer Synthesis. *3-Arm ABC μ-Star Polymers.* We previously used benzyl bromide function as a reaction site to connect two polymer chains.[9−13] In fact, the benzyl bromide reaction site was found to quantitatively react with a variety of living anionic polymers ranging from highly reactive living PS to less reactive living PMMA. However, one of the major problem was the transformation stage from precursory benzyl alcohol to benzyl bromide function, which required strong acidic conditions. It was actually observed that P^{t}BMA, PBnMA, and most poly(alkyl methacrylate)s having protective functionalities were not stable and partly or even completely decomposed under such acidic conditions. In order to avoid this problem, we have developed PA function and used it as a new reaction site instead of benzyl bromide function in recent papers.[38,68−72] As reported previously, the transformation to PA function was carried out under slightly basic conditions, in which the above

Scheme 3. Synthesis of 3-Arm AA′A″ Star PMMA



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polymers were stable. Therefore, the PA reaction site was used throughout this study. In order to synthesize a variety of well-defined μ-star polymers, we have developed a specially designed DPE derivative substituted with trimethylsilyl (TMS)- and *tert*-butyldimethylsilyl (TBDMS)-protected hydroxyl functionalities, **2**, as a new dual-functionalized core agent. This DPE derivative can progressively offer two reaction sites via two different silyl-protected hydroxyl functionalities and, therefore, can be used for the synthesis of both 3-arm ABC and 4-arm ABCD μ-star polymers. Moreover, **2** is found to be effectively used for the successive synthesis of a series of μ-star polymers by a new iterative methodology, which will be introduced in the next section.

To examine the general utility of **2** as a dual-functionalized core agent in the synthesis of 3-arm μ-star polymers, a 3-arm AA′A″ star-branched PMMA was first synthesized, as illustrated in Scheme 3. The synthesis was initiated to prepare an α-terminal-functionalized PMMA with TMS- and TBDMS-protected hydroxyl functionalities. This polymer was prepared by the living polymerization of MMA in THF at −78 °C for 20 min with the functional DPE anion prepared from **2** and oligo(α-methylstyryl)lithium. In order avoid the attack on the TMS-protected functionality of **2** by *sec*-BuLi, a less reactive and bulkier oligo(α-methylstyryl)lithium was used. A 3-fold excess of LiCl was added prior to the polymerization to narrow the molecular weight distribution of the resulting PMMA. It is common known that TMS-protected functionality is deprotected under milder conditions than TBDMS one. In practice, the TMS-protected functionality was readily and completely deprotected to generate a hydroxyl group by pouring the polymer into methanol containing a few drops of acetic acid, while the TBDMS-protected functionality was stable under such conditions. The hydroxyl group was converted to a PA function by the Mitsunobu esterification reaction with α-phenylacrylic acid. The conversion was confirmed to be virtually quantitative by the ^{1}H NMR spectrum, where new signals corresponding to vinylene protons of the PA function appeared at 6.31 and 5.87 ppm with the expected integral ratios. Moreover, the benzyl protons were completely shifted from 4.62 to 5.19 ppm, also strongly indicating a quantitative conversion. The resulting chain-end-(PA and TBDMS-protected hydroxyl)-functionalized PMMA was reacted with a 3-fold excess of living PMMA, separately prepared, in THF at −40 °C for 20 h.

The reaction was terminated with degassed methanol, and the reaction mixture was precipitated in hexane. The SEC profile exhibits only two peaks for the linked product and the deactivated living PMMA used in excess in the reaction, as shown in Figure 3a. The linking efficiency was estimated to be almost quantitative by comparing these two peak areas. The linked polymer was isolated in 80% yield by fractional precipitation, reprecipitated twice, and freeze-dried from its absolute benzene solution. The isolated polymer possessed a sharp monomodal SEC distribution (see Figure 3b). The M_n value (26.2 kg/mol) observed by SEC-RALLS was in good agreement with that calculated (M_n = 25.3 kg/mol). Neither oligomerization nor even dimerization of the PA function with the produced enolate anion occurred under the conditions employed.

The TBDMS-protected functionality which remained between two PMMA segments was deprotected by treatment with a 30-fold excess of $(C_4H_9)_4NF$ in THF at −10 °C for 10 h. The hydroxyl group thus generated was also converted to the

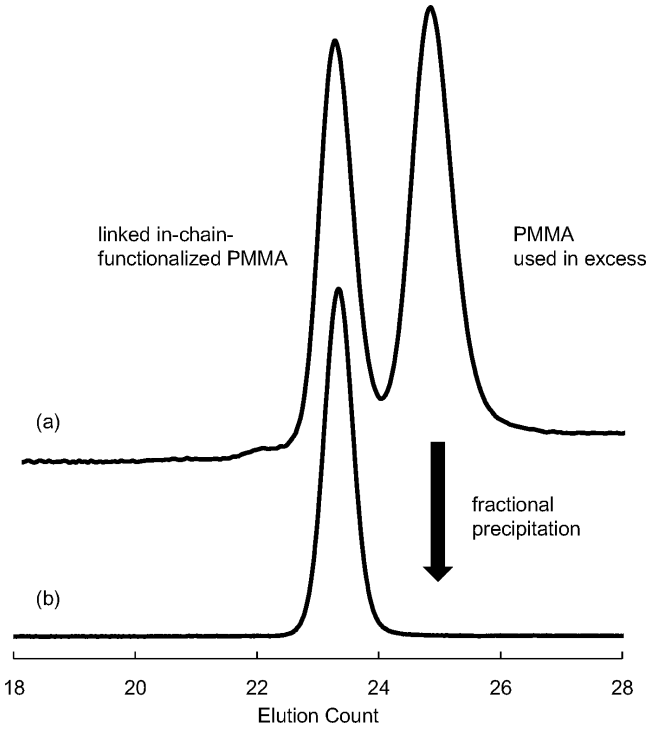

Figure 3. SEC profiles of the polymer mixture obtained by the linking reaction (a) and the linked polymer after fractional precipitation (b).

PA function in the same manner mentioned above. Then, a 3-fold excess of living PMMA, separately prepared, was reacted with the resulting in-chain-PA-functionalized PMMA. The SEC profile of the reaction mixture exhibited only two peaks for the linked product and the deactivated living PMMA used in excess, and the reaction efficiency was ca. 100% based on the two peak areas (see Figure 4a). Moreover, the peak for the in-chain-PA-functionalized PMMA was not present, indicating also the complete linking reaction. The linked polymer isolated in 80% yield by fractional precipitation possessed an M_n value (36.8 kg/mol), measured by RALLS, in agreement with that predicted (34.8 kg/mol) and a narrow molecular weight distribution (M_w/M_n = 1.03) (see Figure 4b). These results clearly indicate the successful synthesis of the target 3-arm AA′A″ star PMMA with well-defined structures. Thus, **2** satisfactorily worked as the dual-functionalized core agent in the synthesis of 3-arm star-branched PMMA.

This method of using **2** was next applied to the synthesis of 3-arm ABC μ-stars. The same aforementioned PMMA α-terminal-functionalized with two different silyl-protected hydroxyl functionalities was used as the starting polymer. The first reaction sequence (selective deprotection of the TMS-protected functionality, conversion to the PA function used as the reaction site, and the linking reaction with a 3-fold excess of living poly(ethyl methacrylate) (PEMA)), followed by the second reaction sequence (deprotection of the TBDMS-protected functionality, conversion to the PA function, and the linking reaction with a 3-fold excess of living poly(*tert*-butyl methacrylate) (P^{t}BMA)), was carried out under identical conditions except for the linking reaction between living P^{t}BMA and in-chain-PA-functionalized PMMA-*b*-PEMA, which was performed at −25 °C for 20 h. As expected, both reaction sequences proceeded cleanly and quantitatively. The final polymer isolated by SEC fractionation was observed to have a sharp monomodal distribution (M_w/M_n = 1.07). The M_n values

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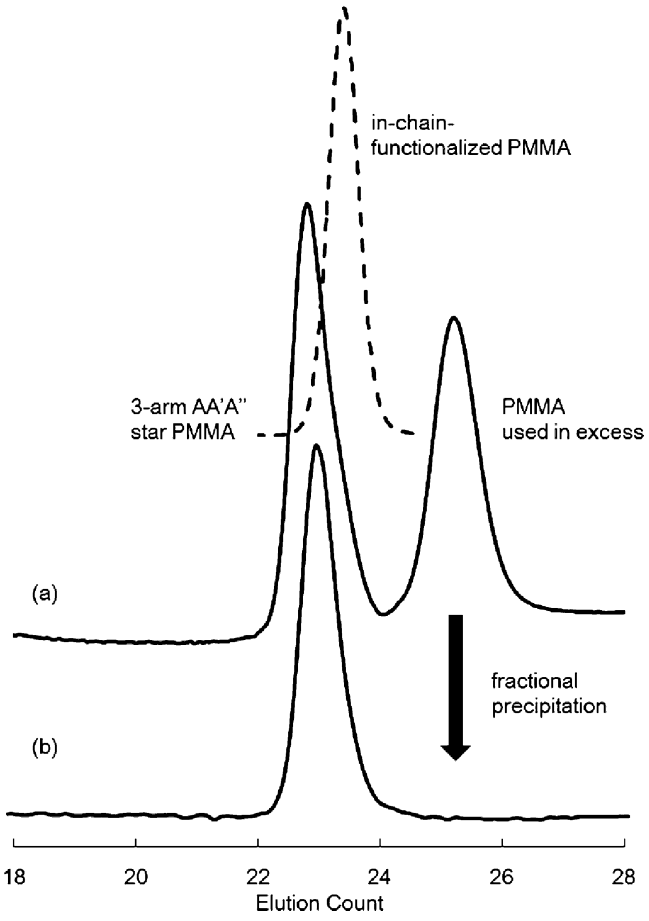

Figure 4. SEC profiles of the polymer mixture obtained by the linking reaction (a) and 3-arm AA′A″ star PMMA after fractional precipitation (b).

observed by RALLS and ^{1}H NMR agreed with that calculated, as listed in Table 4. Furthermore, agreement between the compositions observed by ^{1}H NMR and that calculated was satisfactory. Thus, a new 3-arm ABC μ-star polymer composed of PMMA, PEMA, and P^{t}BMA was successfully synthesized.

It was also possible to synthesize another 3-arm ABC μ-star polymer consisting of P^{t}BMA, P(Si-HEMA), and P(acetal-DIMA) segments by carrying out similar reaction sequences. The synthesis started from P^{t}BMA α-terminal-functionalized with TMS- and TBDMS-protected hydroxyl functionalities, which was prepared by the polymerization of ^{t}BMA with the functional DPE anion prepared from **2** and oligo(α-methylstyryl)lithium in the presence of a 3-fold excess of LiCl in THF at −78 °C for 5 h. The TMS-protected functionality was selectively deprotected in methanol containing a few drops of acetic acid, and the generated hydroxyl group was converted to the PA function by the Mitsunobu esterification reaction. Then, a 3-fold excess of living P(acetal-DIMA) was reacted with the α-terminal-(PA and TBDMS-protected hydroxyl)-functionalized P^{t}BMA in THF at −40 °C for 20 h. The resulting polymer was treated with a 30-fold excess of $(C_4H_9)_4NF$ in THF at −10 °C for 20 h. With this treatment, the TBDMS-protected functionality was deprotected to generate the hydroxyl group, while the acetal-protected functionality of P(acetal-DIMA) was stable and remained completely intact under the conditions. The hydroxyl group was converted to the PA function. Finally, a 3-fold excess of living P(Si-HEMA) was reacted with the in-chain-PA-functionalized P^{t}BMA-*b*-P(acetal-DIMA) at −40 °C for 20 h.

The resulting polymer is of special interest in terms of functionality because it can be converted to a new functional 3-arm ABC μ-star polymer composed of poly(2-hydroxyethyl methacrylate) (PHEMA), poly(2,3-dihydroxypropyl methacrylate) (PDIMA), and poly(methacrylic acid) segments by progressively treating it with $(C_4H_9)_4NF$, 2 N HCl, followed by $(CH_3)_3SiCl$/LiBr. It should herein be mentioned that both of the above two polymers are the first successful well-defined 3-arm ABC μ-star polymers composed of three different methacrylate-based polymer segments.

A 3-arm ABC μ-star polymer consisting of PMMA, PS, and P2VP segments could also be synthesized by the method of using **2**. The synthesis started from the same PMMA α-terminal-functionalized with two different silyl-protected hydroxyl functionalities as that used above. A 1.5-fold excess of living PS end-capped with DPE and a 2-fold excess of living P2VP were reacted in the first and second linking reaction steps. Because of the higher nucleophilicity of both living polymers, the reactions were carried out in THF at −78 °C in order to avoid undesirable side reactions, such as ester and C═N bond attack by their chain-end anions. The target 3-arm ABC μ-star-branched polymer composed of PMMA, PS, and P2VP segments was successfully synthesized without difficulty. This successful synthesis clearly demonstrates that the PA function is a very convenient reaction site, capable of reacting with all of three living polymers having quite different chain-end reactivity (or nucleophilicity).

Like DPE, the DPE derivative, **2**, reacted quantitatively with living PS (poly(styryllithium) (PSLi)) in a 1:1 addition manner

Table 4. Characterization Results of 3-Arm ABC μ-Star Polymers

polymer segments			M_n (kg/mol)			M_w/M_n	composition (wt %)[a]	
A	B	C	calcd	RALLS[b]	^{1}H NMR	SEC[c]	calcd	^{1}H NMR
PMMA	PMMA	PMMA	34.8	36.8		1.03		
PMMA	PEMA	P^{t}BMA	30.8	32.4	28.4	1.07	38/30/32	39/28/33
P^{t}BMA	PDIMA	PHEMA	48.5	51.3	49.4	1.04	49/17/34	48/15/37
PMMA	PS	P2VP	34.9	41.3	35.6	1.05	24/35/41	22/34/44
PS	PMMA	PEMA	33.6	35.2	33.8	1.04	37/34/29	37/37/26
PS	PMMA	P^{t}BMA	31.0	31.2	31.7	1.03	34/36/30	32/37/31
PS	PMMA	PDIMA	31.5	31.7	31.1	1.04	34/37/29	33/37/30
PS	P2VP	P^{t}BMA	30.5	32.5	28.1	1.04	41/28/31	41/29/30
PS	P2VP	PMOS	30.1	30.0	30.1	1.04	42/28/30	43/30/27

[a]A/B/C polymer segments. [b]Determined by SEC with triple detectors. [c]Determined by SEC using PS standards.

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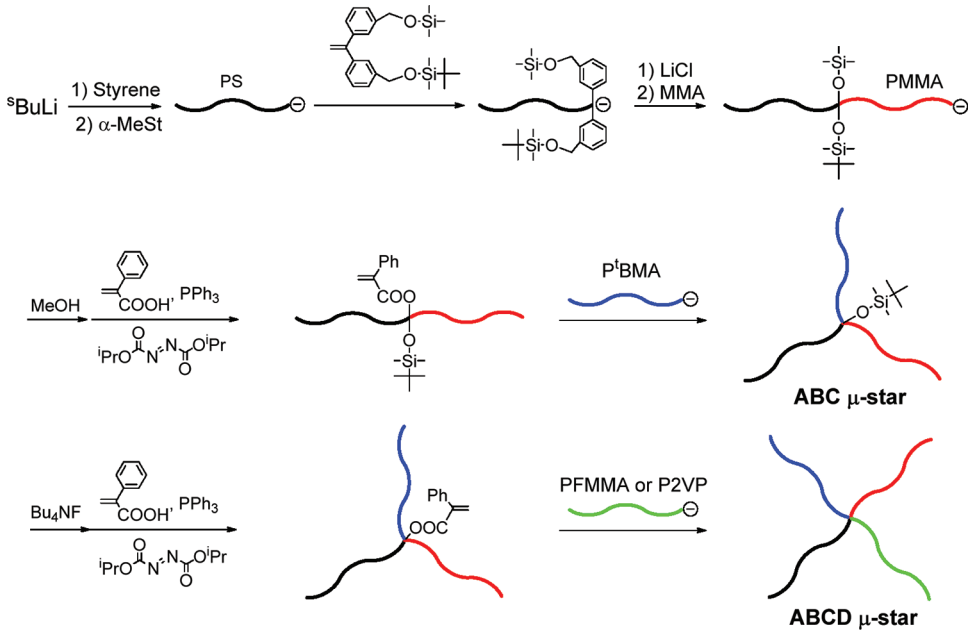
Scheme 4. Synthesis of 4-Arm ABCD μ-Star Polymer



in THF at −78 °C to introduce two different silyl-protected hydroxyl functionalities at the ω-chain-end. In this reaction, PSLi was end-capped with a few units of α-methylstyrene in order to avoid the attack on the TMS-protected functionality of **2** by PSLi, similar to the case using *sec*-BuLi. The TMS-protected functionality was deprotected by pouring the polymer into methanol containing a few drops of acetic acid, and the generated hydroxyl group was converted to the PA function. The resulting ω-chain-end-(PA and TBDMS-protected hydroxyl)-functionalized PS was reacted with a 3-fold excess of living PMMA at −40 °C for 20 h to afford an in-chain-(TBDMS-protected hydroxyl)-functionalized PS-*b*-PMMA. Subsequently, the TBDMS-protected hydroxyl functionality was deprotected with $(C_4H_9)_4NF$ at −10 °C, and the hydroxyl group generated was converted to the PA function. The in-chain-PA-functionalized PS-*b*-PMMA thus prepared was reacted with either of a 3-fold excess of living PEMA, P^{t}BMA, or P(acetal-DIMA) at −40 °C for 20 h, resulting in three ABC μ-star polymers, composed of PS, PMMA, and one of the above methacrylate-based polymer segments. Their well-defined and expected structures were confirmed by SEC, RALLS, and ^{1}H NMR analyses, as listed in Table 4. Similarly, two more 3-arm ABC μ-stars composed of PS, P2VP, P^{t}BMA, PS, and P2VP, poly(4-methoxystyrene) (PMOS) could be synthesized by the linking reaction of in-chain-PA-functionalized PS-*b*-P2VP with a 3-fold excess of living P^{t}BMA at −25 °C for 20 h and with a 1.5-fold excess of living PMOS at −78 °C for 10 h (see also Table 4).

In the synthesis of 3-arm ABC μ-star polymers by the method using **2**, the addition order of living anionic polymer to be reacted in the reaction sequence is not limited and any order is acceptable. The only exception is the use of living P(Si-HEMA), since selective deprotection of the TBDMS-protected functionality of **2** is not possible in the presence of P(Si-HEMA) segment having the same TBDMS-protected functionalities in the side chain. Therefore, this living polymer must be used in the final linking reaction step. Thus, the general utility of **2** as a dual-functionalized core agent is obvious, and the synthetic method of using **2** in conjunction with the living anionic polymerization system becomes a versatile synthetic procedure, with which a variety of well-defined 3-arm ABC μ-star polymers can be synthesized. Most of these polymers herein synthesized, composed of all different methacrylate-based polymers or PS, P2VP, and methacrylate-based polymers, are new μ-star polymers which are difficult to synthesize by any other method.

4-Arm ABCD μ-Star Polymers. As mentioned in the Introduction, only a few successful examples of well-defined 4-arm ABCD μ-stars, synthesized by living anionic polymerization, have so far been reported.[43−46] With the above method of using **2**, the synthesis of 4-arm ABCD μ-star polymers is also possible, as illustrated in Scheme 4. In this synthesis, the first step involves the reaction of PSLi end-capped with a few units of α-methylstyrene with **2**, followed by the polymerization of MMA, to prepare PS-*b*-PMMA in-chain-functionalized with TMS- and TBDMS-protected hydroxyl functionalities. Similar to the above method, the first reaction sequence (selective deprotection of the TMS-protected functionality, conversion to the PA function, and the linking reaction with a 3-fold excess of living P^{t}BMA at −25 °C for 20 h) was carried out to result in a 3-arm ABC μ-star polymer core-functionalized with a TBDMS-protected functionality. Then, the second reaction sequence (deprotection of the TBDMS-protected functionality, conversion of the hydroxyl group to the PA reaction site, and the linking reaction with a 3-fold excess of living poly(ferrocenylmethyl methacrylate) (PFMMA)) yielded a target 4-arm ABCD μ-star polymer. As can be seen in Figure 5a, the SEC profile exhibits only two peaks corresponding to the linked product and the deactivated living PFMMA used in excess in the reaction, and the peak corresponding to the 3-arm ABC star disappears. This clearly indicates that the linking reaction was quantitative under such conditions. The linked polymer was isolated by SEC fractionation (see Figure 5b) and characterized by SEC, RALLS, and ^{1}H NMR analyses. The results are summarized in Table 5.

It was observed that the isolated polymer possessed a sharp monomodal SEC distribution (M_w/M_n = 1.03). The molecular weights determined by RALLS and ^{1}H NMR ($M_{n,RALLS}$ = 42.7

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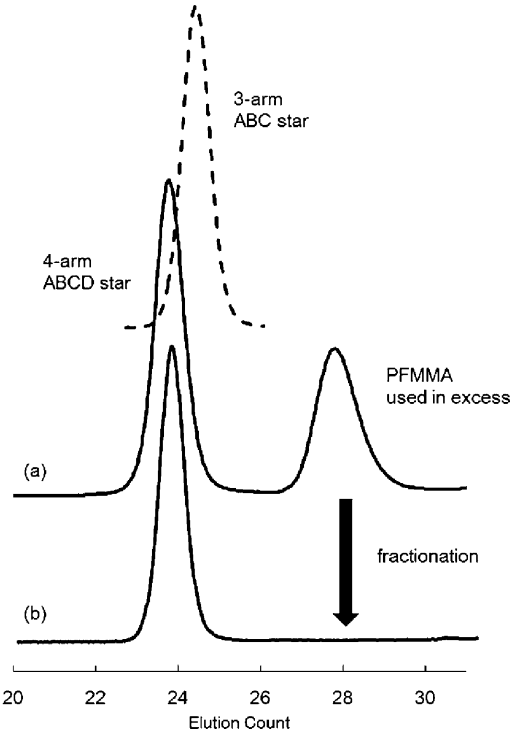

Figure 5. SEC profiles of the polymer mixture obtained by the linking reaction (a) and 4-arm ABCD μ-star polymer after SEC fractionation (b).

and $M_{n,NMR}$ = 41.1 kg/mol) were in good agreement with that calculated (M_n = 41.4 kg/mol). Moreover, the composition observed by ^{1}H NMR was consistent with that calculated from the feed ratio. Thus, a new 4-arm ABCD μ-star polymer composed of PS and three different methacrylate-based polymer segments (PMMA, P^{t}BMA, and PFMMA) was successfully synthesized. One more 4-arm ABCD μ-star could also be synthesized by the linking reaction of the above core-PA-functionalized 3-arm ABC μ-star with a 2-fold excess of living P2VP at −78 °C for 10 h. By analogy with the synthesis of 3-arm ABC μ-stars, **2** also plays a key role as a dual-functionalized core agent in the synthesis of 4-arm ABCD μ-star polymers.

Successive Synthesis of μ-Star Polymers with up to 5 Arms by a New Iterative Methodology. In the preceding section, we demonstrated the general utility of **2** in the synthesis of both 3-arm ABC and 4-arm ABCD μ-star polymers. However, μ-star polymers having more arms cannot be synthesized by the above method. The reason is that the PA reaction site disappears after the final linking reaction, and the arm segment can no longer be introduced into the star. In order to further synthesize μ-star polymers having five or more arms, we have herein developed a new iterative methodology, conceptually similar to those previously reported by our group.[11−13,47−49] As described in the Introduction, the reaction system of the iterative methodology is designed in such a way that the same reaction site is always regenerated after the introduction of an arm segment in each reaction sequence and this reaction sequence consisting of "arm introduction and regeneration of the same reaction site" is repeatable. Accordingly, the arm segments can be successively and, in principle, limitlessly introduced by repeating the reaction sequence.

The proposed new iterative methodology is illustrated in Scheme 5. The synthesis was initiated from the same α-terminal PMMA functionalized with TMS- and TBDMS-protected hydroxyl functionalities as that often used in the synthesis of 3-arm μ-star polymers. The first reaction sequence involves the selective deprotection of the TMS-protected functionality, conversion of the generated hydroxyl group to the PA function, and the linking reaction with a 3-fold excess of living PEMA. An in-chain-(TBDMS-protected hydroxyl)-functionalized PMMA-*block*-PEMA was obtained at this stage. Then, the TBDMS-protected functionality was deprotected with $(C_4H_9)_4NF$ to generate the hydroxyl group, followed by conversion to the PA function.

The PA function thus regenerated in the PMMA-*b*-PEMA was reacted with a 2-fold excess of the functional DPE anion prepared from **2** and oligo(α-methylstyryllithium) at −78 °C for 30 min, used as the initiator in the polymerization of MMA. The reaction was confirmed to be virtually quantitative by ^{1}H NMR analysis. These reaction steps are also involved in the first reaction sequence (or the first iterative process).

A key point of the first sequence was the reaction between the PA reaction site regenerated via the TBDMS-protected functionality and the functional DPE anion to introduce the TMS- and TBDMS-protected hydroxyl functionalities. Accordingly, the resulting PMMA-*b*-PEMA is the same in chain-functionality as the starting PMMA, except for the PEMA segment. By using two different silyl-protected functionalities, the same reaction sequence (selective deprotection of the TMS-protected hydroxyl functionality, conversion of the hydroxyl group to the PA function, the linking reaction of a 3-fold excess of living P^{t}BMA at −25 °C for 20 h, deprotection of the TBDMS-protected functionality, conversion of the hydroxyl group to the PA function, and the reaction of the PA reaction site with a 2.0-fold excess of the functional DPE anion) could be repeated. As a result, a 3-arm ABC μ-star polymer core-functionalized with TMS- and TBDMS-protected hydroxyl functionalities, composed of PMMA, PEMA, and P^{t}BMA segments, was synthesized. Once again, the final reaction step between the PA reaction site and the functional DPE anion is the key to further continuing the same reaction sequence. In practice, a 4-arm ABCD μ-star polymer, followed by a 5-arm ABCDE μ-star polymer, was successively synthesized by repeating the same reaction sequence two more times. Living poly(benzyl methacrylate) (PBnMA) and poly(2-methoxyethyl methacrylate) (PMOEMA) were sequentially reacted to introduce the D and E segments, respectively.

Table 5. Characterization Results of 4-Arm ABCD μ-Star Polymers

polymer segments		M_n (kg/mol)			M_w/M_n	composition (wt %)[a]	
A/B/C	D	calcd	RALLS[b]	^{1}H NMR	SEC[c]	calcd	^{1}H NMR
PS/PMMA/P^{t}BMA	PFMMA	41.4	42.7	41.1	1.03	26/28/23/23	27/30/21/22
PS/PMMA/P^{t}BMA	P2VP	41.7	42.9	39.9	1.04	25/26/23/26	26/27/23/24

[a]A/B/C/D polymer segments. [b]Determined by SEC with triple detectors. [c]Determined by SEC using PS standards.

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Scheme 5. Successive Synthesis of μ-Star Polymers by a New Iterative Methodology

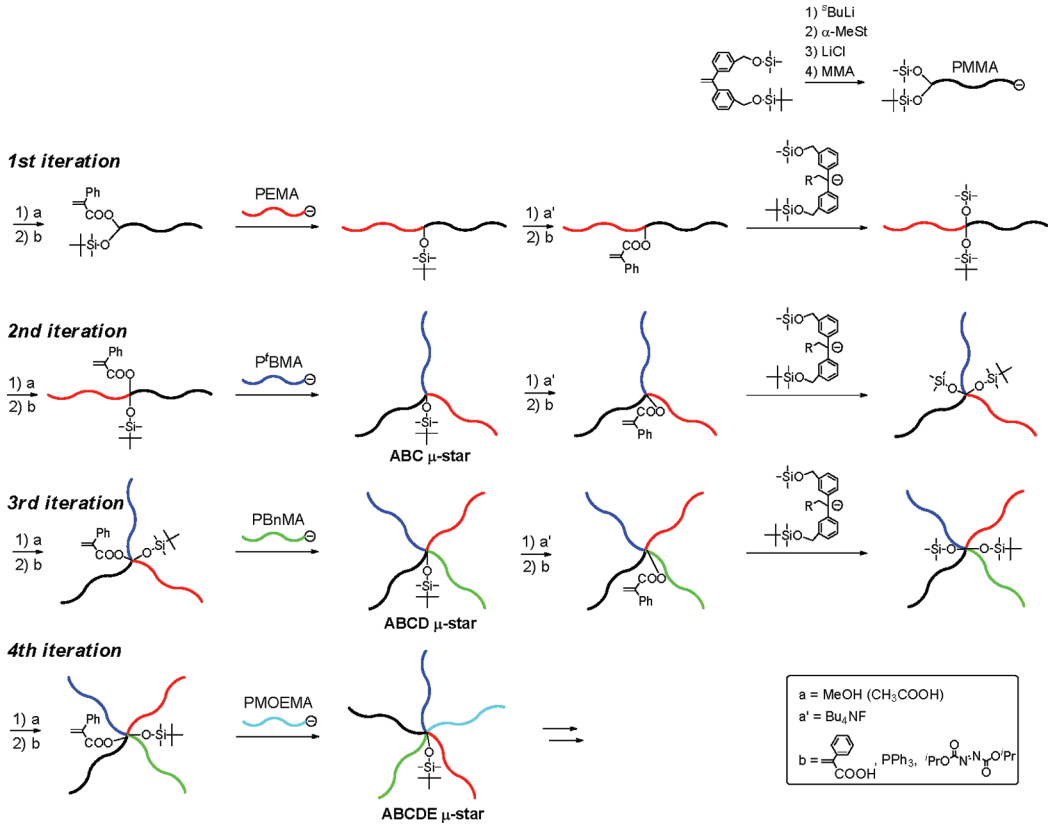

Table 6. Synthesis of μ-Star Polymers by a New Iterative Methodology

	M_n (kg/mol)			M_w/M_n	composition (wt %)[a]	
μ-star	calcd	RALLS[b]	^{1}H NMR	SEC[c]	calcd	^{1}H NMR
ABC[d]	32.2	33.8	32.3	1.03	38/31/31	37/32/31
ABCD[d]	43.4	43.0	43.2	1.03	30/25/22/23	30/26/20/24
ABCDE[d]	52.0	51.5	51.6	1.03	24/21/18/19/18	26/20/16/20/18
ABCD[e]	39.3	41.2	38.4	1.03	28/30/22/20	26/29/23/22
ABCDE[e]	51.7	52.7	50.2	1.04	21/23/17/17/22	21/24/16/17/22

[a]A/B/C/D/E polymer segments. [b]Determined by SEC with triple detectors. [c]Determined by SEC using PS standards. [d]A/B/C/D/E = PMMA/PEMA/P^{t}BMA/PBnMA/PMOEMA. [e]A/B/C/D/E = PS/PMMA/P^{t}BMA/P4MS/PBnMA.

The characterization results are summarized in Table 6. In the 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE μ-star polymers, their molecular weights determined by RALLS and ^{1}H NMR are in good agreement with those calculated from monomer to initiator ratios and narrow molecular weight distributions are attained. Furthermore, their observed compositions are consistent with those calculated. These results clearly indicate the successful synthesis of target μ-star polymers with well-defined and expected structures. For comparison, all SEC peaks for A, AB, 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE μ-star polymers are shown in Figure 6. It should be mentioned that the resulting polymers are quite new and the first successfully synthesized μ-star polymers composed of all different methacrylate-based arm segments. Since the final 5-arm μ-star still possesses the TBDMS-protected functionality which is convertible to the PA reaction site at the core, it may be possible to continue the same reaction sequence.

As often mentioned above, the key step of the iterative methodology is the reaction between the PA reaction site regenerated via the TBDMS-protected functionality and the functional DPE anion in order to introduce both the TMS- and the TBDMS-protected hydroxyl functionalities. Interestingly and importantly, another route exists for the introduction of two such silyl-protected functionalities. As illustrated in Scheme 6, living anionic poly(4-methylstyrene) (P4MS), like living PS mentioned in the preceding section, readily reacts with **2** in a 1:1 addition manner to introduce two silyl-protected hydroxyl functionalities at the chain-end, and the chain-end anion is changed to the DPE anion, which is exactly the same in structure as the functional DPE anion. Accordingly, this chain-end-functionalized living P4MS with **2** is expected to react with a chain-PA-functionalized polymer to introduce two silyl-protected hydroxyl functionalities. More importantly, the iterative methodology can be started from the resulting polymer having two silyl-protected functionalities.

A typical example is shown in Scheme 7, in which a 4-arm ABCD, followed by a 5-arm ABCDE μ-star polymer, can be synthesized by the method using a chain-end-functionalized living P4MS with two silyl-protected functionalities and the

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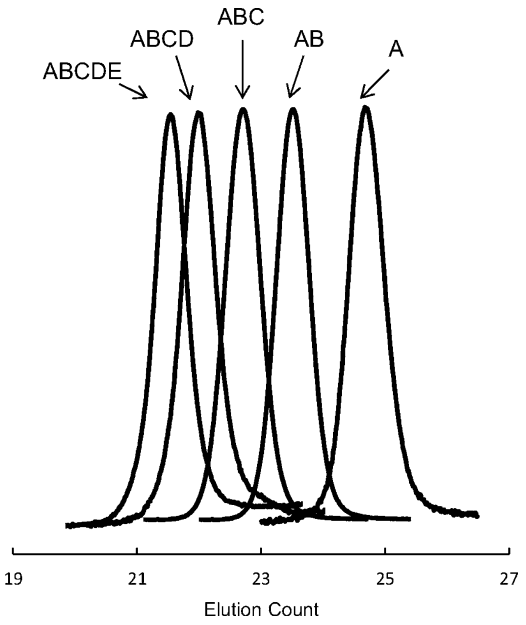
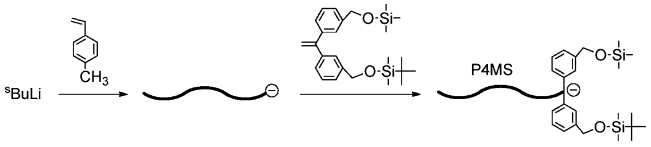


Figure 6. SEC profiles of A, AB, 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE μ-star polymers synthesized by a new iterative methodology.

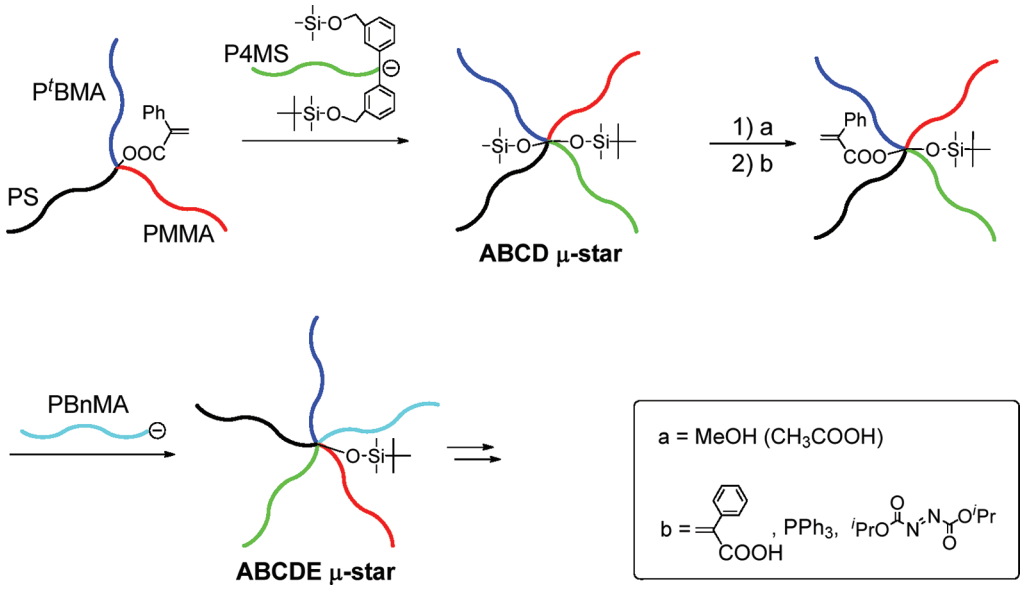
Scheme 6. 1:1 Addition Reaction of Living P4MS with 2



core-PA-functionalized ABC μ-star polymer composed of PS, PMMA, and P^{t}BMA synthesized in the preceding section (see Scheme 4). Poly(4-methylstyryl)lithium (P4MSLi) was first prepared by the living anionic polymerization of 4-methylstyrene with *sec*-BuLi in THF at −78 °C for 1 h, and a 2.0-fold excess of **2** was subsequently reacted *in situ* to introduce both the TMS- and the TBDMS-protected hydroxyl functionalities at the chain-end. The resulting chain-end-functionalized P4MSLi with **2** was *in situ* reacted with the core-PA-functionalized 3-arm ABC μ-star at −78 °C for 10 h to link the P4MS chain to the star, resulting in a 4-arm ABCD μ-star polymer core-functionalized with two silyl-protected hydroxyl functionalities. The TMS-protected functionality was selectively deprotected by pouring the polymer into methanol containing a few drops of acetic acid, and the generated hydroxyl group was converted to the PA function. Then, a 3-fold excess of PBnMA was reacted with the resulting core-(PA and TBDMS-protected hydroxyl)-functionalized 4-arm ABCD μ-star at −40 °C for 20 h. Under such conditions, the reaction was complete and yielded a 5-arm ABCDE μ-star composed of PS, PMMA, P^{t}BMA, P4MS, and PBnMA segments. The expected and well-defined structure of the polymer was confirmed by the analytical results listed in Table 6. Thus, the chain-end-functionalized P4MSLi with **2** could also be utilized in the methodology. The use of this functionalized living polymer is advantageous to introduce one arm segment in addition to the two silyl-protected functionalities, and therefore, one linking reaction step can be skipped.

In summary, the proposed iterative methodology proves effective to successively synthesize a series of μ-star polymers with many arms and can continue via the two different silyl-protected functionalities introduced by reacting of the regenerated PA reaction site with either the DPE anion prepared from **2** or the living P4MS (and possibly living polymers of styrene and its derivatives) end-functionalized with **2**. One more important issue to be emphasized in this study is to use the PA function as the reaction site, which is capable of reacting with a variety of living anionic polymers from living PS, P2VP, to PMMA or other poly(alkyl methacrylate)s with different chain-end nucleophilicities. Accordingly, the iterative methodology allows access to a wide variety of well-defined μ-star polymers composed of not only methacrylate-based polymers but also PS and P2VP segments.

Scheme 7. Successive Synthesis of 4-Arm ABCD and 5-Arm ABCDE μ-Star Polymers by an Iterative Methodology Using Living P4MS Chain-End Functionalized with 2



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CONCLUSIONS

We have demonstrated the general utility of the DPE derivative substituted with TMS- and TBDMS-protected hydroxyl functionalities, **2**, as a new dual-functionalized core agent in conjunction with the living anionic polymerization system for the synthesis of various well-defined 3-arm ABC and 4-arm ABCD μ-star polymers. Two different protected hydroxyl functionalities were progressively deprotected to generate hydroxyl groups, followed by conversion to the PA functions at separate stages, and the PA functions were reacted with appropriate living anionic polymers to result in the above μ-stars.

A new iterative methodology using the functional DPE anion prepared from **2** and oligo(α-methylstyryl)lithium has been developed in order to synthesize a series of μ-stars with up to five. The key step of the methodology is the reaction between the PA reaction site regenerated from the TBDMS-protected functionality and the functional DPE anion to introduce both the TMS- and the TBDMS-protected hydroxyl functionalities. With the use of two such different silyl-protected hydroxyl functionalities, the reaction sequence consisting of "arm introduction and regeneration of the PA reaction site" is achieved and repeated several times to successively synthesize quite new 3-arm ABC, 4-arm ABCD, and 5-arm ABCDE μ-star polymers composed of all different methacrylate-based polymer segments. Both the TMS- and the TBDMS-protected hydroxyl functionalities could also be introduced by using P4MSLi end-functionalized with **2**. This demonstrates another possibility for starting the same iterative methodology. One more advantage of the synthetic procedures developed in this study is to use the PA function as the reaction site, which is capable of reacting with a variety of living anionic polymers with different chain-end nucleophilicities. This enables the synthetic range of μ-star polymers to be significantly broadened.

ASSOCIATED CONTENT

Supporting Information

Text giving the syntheses of chain-end-PA-functionalized PS and other chain-end-functionalized (PS)s, the synthesis of 3-arm ABC μ-star polymers, and the successive synthesis of μ-star polymers by using living P4MS chain-end-functionalized with **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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(67) The polymerization of ^{t}BMA was slow and took a few hours to be completed at −78 °C. It was already observed that the living P^{t}BMA is stable enough for 20 h at −78 °C. The postpolymerization was carried out to check the stability of living P^{t}BMA at −40 °C for 2 h as follows: ^{t}BMA was polymerized in THF at −78 °C for 5 h with the initiator prepared from DPE and *sec*-BuLi, and the polymerization mixture was allowed to stand at 40 °C for 2 h. Then, the mixture was cooled to −78 °C, and ^{t}BMA precooled at −78 °C was added to the mixture to carry out the postpolymerization at −78 °C for 5 h. The polymers were recovered by precipitation in a mixture of methanol and water, and the recovered polymers were analyzed by SEC-RALLS to measure their peak areas and absolute molecular weights. The stability was evaluated by comparing SEC peak areas and molecular weight values of the P^{t}BMA obtained by the first polymerization and the postpolymer. Similarly, postpolymerizations were carried out under various conditions by the same experimental operation as that described.
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