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ARTICLE

Synthesis of Well-Defined Miktoarm Star-Branched Polymers Consisting of Perfluorinated Segments by a Novel Methodology Using Soluble In-Chain-Benzyl Bromide-Functionalized AB Diblock Copolymers as Key Building Blocks

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ABSTRACT: In order to synthesize miktoarm star-branched polymers consisting of poly(2-(perfluorooctyl)-ethyl methacrylate) (P(F_8H_2−MA)) segments insoluble in most organic solvents, a novel methodology based on a new concept by using a THF-soluble in-chain-benzyl bromide (BnBr)-functionalized AB diblock copolymer, polystyrene (PS)-*block*-P(F_8H_2−MA), as a key building blocks is proposed. The methodology involves the following three reaction steps: (1) preparation of in-chain-(3-*tert*-butyldimethylsilyloxymethyl-phenyl) (SiOMP)-functionalized PS-*block*-P(F_8H_2−MA) by means of living anionic polymerization, (2) a transformation reaction of the SiOMP group into BnBr function, and (3) a coupling reaction of the resulting in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) with another living anionic polymer(s). With this methodology, a variety of well-defined 3-arm ABC, 4-arm A_3B, ABC_2, and ABCD miktoarm star-branched polymers consisting of P(F_8H_2−MA) (B) segments was successfully synthesized. Thus, the proposed methodology satisfactorily works and opens a new route for the synthesis of miktoarm star-branched polymers consisting of insoluble arm segment(s).

Introduction

Perfluoro- or semifluoroalkyl groups represented as $CF_3(CF_2)_{m-1}(CH_2)_n$ (abbreviated as F_mH_n) have attracted much attention due to their unique and interesting characteristics, originating from the C−F bond as well as the F atom.[1−3] Among them, long chain fluorinated F_mH_n groups with "*m*" of higher than 8 in number are well-known as nanoscale rigid rod-like molecules with a helical conformation, capable of forming a liquid crystalline phase in air−water interface as well as in the bulk.[4−12] The resulting phases exhibit strong hydrophobicity and oleophobicity, excellent chemical and thermal stabilities, low adhesion and low friction coefficients, and extremely low surface energies that quite differ substantially from those based on the corresponding hydrocarbons.[13−24]

In order to prepare functional materials utilizing such characteristics of these F_mH_n groups, several kinds of fluorinated (FL) polymers composed of flexible backbones and F_mH_n side chains have so far been synthesized. However, unfortunately, FL polymers with long F_mH_n side chains ($m \geq 8$) are usually practically insoluble in most organic solvents, making them very difficult to directly use. As one of the solutions to overcome such limitation, a variety of chain-end-F_mH_n-functionalized polymers[25−33] and random and block copolymers,[4−8,25−27,34−39] in which F_mH_n groups are incorporated into additional polymer chains to promote the solubilities, have been often employed instead of homopolymers. In fact, improved solubilities of such polymers permit examination of the basic roles of the F_mH_n side chains and utilization of their interesting characteristics in material science. In general, the F_mH_n side chains tend to segregate strongly from the backbone chains and additional polymer chains at the molecular level, followed by self-organization, to form well-oriented liquid crystalline phases at polymer surfaces as well as in the bulk. Moreover, chain-end-F_mH_n-functionalized polymers and block copolymers consisting of F_mH_n-functionalized segments self-organize in water and selective solvents to produce various molecular assemblies such as monolayers, bilayers, regular and reversed micelles and vesicles.[40−53] Thus, the surface, solution, and bulk structures and properties of FL polymers based on their unique characteristics and self-organization are of particular interest.

In contrast to numerous studies using FL block copolymers and chain-end-F_mH_n-functionalized polymers, little has been reported on FL miktoarm star-branched polymers possibly due to the insolubility of F_mH_n-functionalized polymer segments,[54] although effects of star-branched architecture and topology on surface, solution, and bulk structures and properties may possibly be very interesting. Furthermore, the insolubility of F_mH_n-functionalized segment is also a serious problem in the synthesis of such FL miktoarm star-branched polymers, because most of the methodologies effective for the synthesis of well-defined miktoarm star-branched polymers can not be directly applied to the synthesis.[55−59] Herein, we report on a novel methodology based on a new concept using a THF-soluble in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) as a key building block in the synthesis of miktoarm star-branched polymers consisting of F_mH_n-functionalized arm segments which are insoluble in THF.

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Experimental Section

Materials. The reagents (> 98% purities) were purchased from Aldrich Japan and used as received unless otherwise stated. Styrene, α-methylstyrene, 1,1-diphenylethylene (DPE), F_8H_2−MA (98%, Wako Pure Chemicals, Co., Ltd., Japan), 2-vinylpyridine, and methyl methacrylate, THF, chloroform, acetonitrile, $(CH_3)_3SiCl$, LiCl, and LiBr were purified according to the reported procedures described elsewhere.[60,61] Styrene, α-methylstyrene, and DPE were finally distilled in the presence of Bu_2Mg (*ca.* 3−5 mol %) on the vacuum line. Methyl methacrylate was finally distilled from its 3 mol % $(C_2H_5)_3Al$ solution on the vacuum line. 2-Vinylpyridine and F_8H_2−MA were finally distilled over fine powder CaH_2 (after stirring for a few hours) on the vacuum line. Both 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene (**1**) and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)-ethylene (**2**) were synthesized according to our procedures previously reported.[62,63]1,4-Dilithio-1,1,4,4-tetraphenylbutane (**3**) was prepared by the reaction of lithium naphthalenide and DPE in THF at −78 °C for 30 min and used *in situ* in the coupling reaction.

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

Synthesis of In-Chain-SiOMP-Functionalized PS-*block*-P-(F_8H_2−MA) and Transformation Reaction of SiOMP Group into BnBr Function. All of the polymerization and coupling reactions were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors. After the reactors were sealed off from the vacuum line, they were always prewashed with a red-colored 1,1-diphenylhexyllithium in heptane before use. Polystyryllithium (PSLi) was prepared by the polymerization of styrene (22.6 mmol, 2.35 g) in THF solution (25.4 mL) initiated with *sec*-BuLi (0.194 mmol) in heptane solution (2.65 mL) at −78 °C for 20 min. A THF solution (3.20 mL) of **1** (0.397 mmol) was added to the PSLi solution at −78 °C and the reaction mixture was allowed to stand for additional 0.5 h at −78 °C. A small amount of sample was withdrawn to an empty ampule to determine the molecular weight of the polystyrene. Then, LiCl (0.826 mmol) in THF solution (4.75 mL) was added to the reaction mixture at −78 °C and F_8H_2−MA (3.68 mmol, 1.96 g) in THF solution (9.25 mL) precooled at −78 °C was added with vigorous shaking. After the polymerization was allowed to stand for 0.5 h, it was quenched with degassed methanol and the THF solution was poured into a large excess of methanol to precipitate the polymer. The resulting diblock polymer was reprecipitated twice from its THF solution to methanol and freeze-dried from its absolute benzene solution for 48 h. The polymer yield was quantitative (4.06 g). The in-chain-SiOMP-functionalized PS-*block*-P(F_8H_2−MA) thus prepared was characterized by SEC, RALLS, and ^1H NMR. $M_{n,}$ = 24 500 g/mol (^1H NMR) and 25 800 g/mol (RALLS), M_w/M_n = 1.06 (SEC). 300 MHz ^1H NMR ($CDCl_3$, ppm): δ = 7.06−6.42 (broad, aromatics), 4.58 (m, $-C_6H_4-CH_2O$), 4.26 (s, OCH_2-CH_2), 2.45 (s, OCH_2-CH_2), 2.22−1.31 (broad, backbone chains), 1.13 (s, $C-CH_3$), 0.05 (s, $Si(CH_3)_2$).

Under a nitrogen atmosphere, LiBr (16.1 mmol) and $(CH_3)_3SiCl$ (10.1 mmol) was added to the in-chain-SiOMP-functionalized PS-*block*-P(F_8H_2−MA) (4.06 g, 1.74 mmol for SiOMP functionality) dissolved in a mixed solvent of $CHCl_3/CH_3CN$ (30 mL/20 mL) and the reaction mixture was allowed to stir at 40 °C for 24 h. After quenching with a small amount of methanol and removing the solvent, the residual polymer was dissolved in THF and poured into a large amount of methanol to precipitate. The resulting polymer was purified by reprecipitation twice and freeze-drying from its absolute benzene solution. The yield of the polymer was 94% yield (3.80 g, 1.63 mmol for BnBr functionality). The shape and elution count of the polymer obtained after the transformation reaction were almost the same as those before the reaction. The ^1H NMR spectrum showed the complete disappearance of methyl protons (0.05 ppm) of the *tert*-butyldimethylsilyl group as well as methylene protons (4.58 ppm) of the benzyl silyl ether, indicating that the SiOMP group was quantitatively transformed into BnBr function. The benzyl bromide methylene protons were not observed due to the overlapping with the chemical shift (OCH_2-CH_2-) at 4.28 ppm. 300 MHz ^1H NMR ($CDCl_3$, ppm): δ = 7.04−6.43 (broad, aromatics), 4.28 (s, OCH_2-CH_2), 2.47 (s, OCH_2-CH_2), 2.24−1.28 (broad, backbone chains), 1.13 (s, $C-CH_3$).

The synthesis of in-chain-(SiOMP)$_2$-functionalized PS-*block*-P(F_8H_2−MA) and the transformation reaction of the SiOMP groups into BnBr functions were performed in the same manner as those employed as above, except for the using of **2** instead of **1**. M_n = 23 900 g/mol (^1H NMR) and 26 300 g/mol (RALLS), M_w/M_n = 1.06 (SEC). 300 MHz ^1H NMR ($CDCl_3$, ppm): δ = 7.04−6.41 (broad, aromatics), 4.26 (s, OCH_2-CH_2), 2.45 (s, OCH_2-CH_2), 2.21−1.45 (broad, backbone chains), 1.09 (s, $C-CH_3$), 0.05 (s, $Si(CH_3)_2$). In-chain-(BnBr)$_2$-functionalized PS-*block*-P(F_8H_2−MA): 300 MHz ^1H NMR ($CDCl_3$, ppm): δ = 7.05−6.41 (broad, aromatics), 4.25 (s, OCH_2-CH_2), 2.44 (s, OCH_2-CH_2), 2.22−1.26 (broad, backbone chains), 1.09 (s, $C-CH_3$).

General Synthetic Procedure for Miktoarm Star-Branched Polymers. Both 3- and 4-arm miktoarm star-branched polymers were synthesized by the coupling reaction of either in-chain-BnBr- or in-chain-(BnBr)$_2$-functionalized PS-*block*-P(F_8H_2−MA) with a 1.5-fold excess or more excess of living anionic polymer in THF at −40 °C. Although the coupling reaction seemed to be finished within 1 h, the reaction time of 24 h was usually employed by way of precaution. After quenching the reaction with a small amount of degassed methanol, the reaction mixture was poured into a large amount of hexane or methanol to precipitate the polymers. The SEC profile of the crude polymer mixture usually showed two sharp peaks corresponding to the target star and the unreacted living anionic polymer used in excess. By comparing the two SEC peak areas, the coupling efficiency was estimated in each of all cases. The target star-branched polymers were isolated by fractionation using mixed solvents composed of good solvents (benzene, cyclohexane, and THF) and nonsolvents (ethanol and hexane). In general, the high molecular weight stars were precipitated, while lower molecular weight polymers corresponding to the deactivated living anionic polymers remained in the solution. The star-branched polymers were usually isolated in more than 60% yields. The fractionation by SEC was also often employed to completely remove small amounts of lower molecular weight polymers from the stars. The isolated polymers were reprecipitated from their THF solutions to hexane or methanol and freeze-dried from their absolute benzene solutions for 48 h under high-vacuum conditions. The polymers were then characterized by SEC, RALLS, and ^1H NMR to determine their molecular weights, molecular weight distributions, and compositions.

Synthesis of Miktoarm 3-Arm ABC Star−Branched Polymer Composed of PS, P(F_8H_2−MA), and Poly(2-vinylpyridine) (P2VP) Arm Segments. As a representative example, the procedure of the title ABC star synthesis is shown. The living P2VP was prepared by the anionic polymerization of 2VP (11.71 mmol) with *sec*-BuLi (0.114 mmol) in THF (14.8 mL) at −78 °C for 0.5 h.

After it was sampled in a side tube as a reference, the living P2VP (0.0930 mmol) in THF (12.1 mL) was added to a THF solution (23.9 mL) of in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) (0.0465 mmol for BnBr functionality) at −78 °C and the reaction mixture was allowed to react at −40 °C for 24 h. The reaction was terminated with a small amount of degassed methanol and poured into a large excess volume of hexane to precipitate the polymers. The polymers dissolved in benzene was filtrated through a Celite column to remove LiCl, LiBr, and $LiOCH_3$. The target ABC star-branched polymer was isolated by fractional precipitation using a mix solvent including THF and ethanol, purified by reprecipitation from THF to hexanes twice, and finally freeze-dried from its absolute benzene solution for 48 h. The isolated polymer was characterized by SEC, RALLS, and ^{1}H NMR. $M_{n,}$ = 33 300 g/mol (RALLS), M_w/M_n = 1.07 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 8.41−8.12 (m, −N=CH−), 7.21−6.29 (broad, aromatics), 4.25 (s, −O−CH_2−CH_2−), 2.44 (s, −O−CH_2−CH_2−), 2.37−0.95 (broad, backbone chains), 0.95 (s, C−CH_3).

Similarly, the 4-arm ABC_2 star-branched polymer was synthesized under the same conditions. The polymer was isolated in 60% by fractional precipitation using THF and ethanol. $M_{n,}$ = 52 200 g/mol (RALLS), M_w/M_n = 1.07 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 8.39−8.10 (m, −N=CH−), 7.20−6.19 (broad, aromatics), 4.23 (s, −O−CH_2−CH_2−), 2.33 (s, −O−CH_2−CH_2−), 2.37−0.95 (broad, backbone chains), 0.94 (s, C−CH_3).

In order to synthesize 3- and 4-arm miktoarm star-branched polymers composed of PS, P(F_8H_2−MA), and poly(methyl methacrylate) (PMMA) arm segments, the coupling reaction was carried out between either in-chain-BnBr- or in-chain-$(BnBr)_2$-functionalized PS-*block*-P(F_8H_2−MA) and the living PMMA in THF at −40 °C for 24 h. Living PMMA was prepared as follows: At first, *sec*-BuLi (0.108 mmol) in heptane (1.61 mL) was reacted with DPE (0.253 mmol) in THF (2.13 mL) at −78 °C for 0.5 h. After addition of LiCl (0.324 mmol) in THF (3.10 mL) precooled at −78 °C to the reaction mixture, a THF solution (11.3 mL) of MMA (10.9 mmol) was added at once with vigorous shaking at −78 °C. The polymerization was continued in THF at −78 °C for additional 0.5 h. The living PMMA thus prepared was then reacted with in-chain-BnBr- or in-chain-$(BnBr)_2$-functionalized PS-*block*-P(F_8H_2−MA). After quenching the reaction with a small amount of degassed methanol, the mixture was poured into a large amount of methanol to precipitate the polymers in either case. The star-branched polymers were isolated by precipitation of the polymer from its THF solution into a large amount of a mixed solvent (water/ethanol = 1/5 (v/v)), purified by reprecipitation from THF to methanol twice, and freeze-dried from their absolute benzene solutions for 48 h. 3-arm ABC star: M_n = 35 300 g/mol, M_w/M_n = 1.06 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.04−6.40 (broad, aromatics), 4.25 (s, −O−CH_2−CH_2−), 3.62 (s, −OCH_3), 2.44 (s, −O−CH_2−CH_2−), 2.22−1.06 (broad, backbone chains), 0.91 (s, C−CH_3). 4-arm ABC_2 star: M_n = 42 800 g/mol (RALLS), M_w/M_n = 1.04 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.04−6.40 (broad, aromatics), 4.24 (s, −O−CH_2−CH_2−), 3.61 (s, −OCH_3), 2.44 (s, −O−CH_2−CH_2−), 2.21−1.06 (broad, backbone chains), 0.90 (s, C−CH_3).

Synthesis of 4-Arm ABCD Miktoarm Star−Branched Polymer Composed of PS, P(F_8H_2−MA), Poly(α-methylstyrene) (PαMS), and P2VP Arm Segments. α-Methylstyrene (10.1 mmol) was polymerized with *sec*-BuLi (0.0930 mmol) in THF (12.3 mL) at −78 °C for 1.5 h and then reacted with **1** (0.210 mmol) to end-cap the chain-end anion at −78 °C for 20 min. After sampling a small amount of the resulting poly(α-methylstyryl)lithium, in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) (0.0508 mmol for BnBr functionality) in THF (23.5 mL) solution precooled at −78 °C was added to the living polymer solution and the reaction mixture was allowed to react at −40 °C for 24 h. After terminating the reaction with degassed methanol, the reaction mixture was poured into a large amount of methanol to precipitate the polymers. The resulting 3-arm ABC star-branched polymer core-functionalized with SiOMP group was isolated in 85% yield by fractional precipitation using cyclohexane/hexane mixture (1/4, v/v). The isolated polymer was reprecipitated from THF solution to methanol twice and freeze-dried twice from its absolute benzene solution.

The resulting 3-arm ABC star-branched polymer core-functionalized with SiOMP group (0.0230 mmol for SiOMP group) was treated with $(CH_3)_3SiCl$ (1.13 mmol) and LiBr (1.13 mmol) in a mixed solvent of $CHCl_3$ (20 mL) and acetonitrile (15 mL) at 40 °C for 24 h. After quenching the reaction with a small amount of methanol and the solvents were removed, the polymer was purified by reprecipitation using THF and methanol twice and freeze-dried from the absolute benzene solution twice. M_n = 36 300 g/mol (RALLS), M_w/M_n = 1.08 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.04−6.40 (broad, aromatics), 4.25 (s, −O−CH_2−CH_2−), 2.44 (s, −O−CH_2−CH_2−), 2.26−0.60 (broad, backbone chains), 0.95 (s, C−CH_3), 0.46−0.09 (m, α−CH_3−C−C_6H_5).

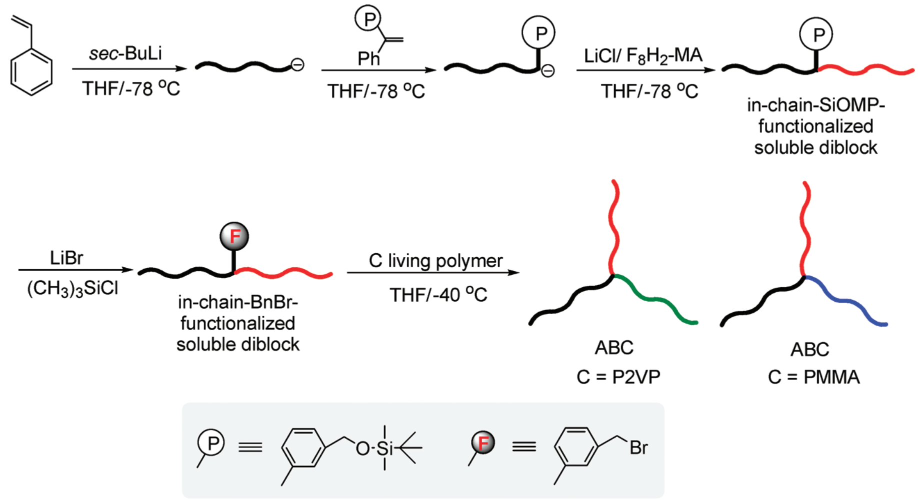
The living P2VP was prepared by polymerization of 2VP (11.85 mmol) with *sec*-BuLi (0.110 mmol) in THF (12.3 mL) at −78 °C for 0.5 h and, after sampling living P2VP, was reacted with the core-BnBr-functionalized 3-arm ABC star-branched polymer (0.0190 mmol) in THF (21.4 mL) at −40 °C for 24 h. After quenching with methanol, the target 4-arm ABCD star-branched polymer was isolated in 86% yield by fractional precipitation using cyclohexane and hexane. Finally, a small amount of a low molecular weight tailing was removed by SEC fractionation. M_n = 46 800 g/mol (RALLS), M_w/M_n = 1.08 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 8.33−8.12 (m, −N=CH−), 7.07−6.41 (broad, aromatics), 4.26 (s, −O−CH_2−CH_2−), 2.43 (s, −O−CH_2−CH_2−), 2.21−0.61 (broad, backbone chains), 0.95 (s, C−CH_3), 0.46−0.10 (m, α−CH_3−C−C_6H_5).

Synthesis of 4-Arm A_2B_2 Miktoarm Star−Branched Polymer Composed of Two PS and Two P(F_8H_2−MA) Segments. Lithium naphthalenide (0.168 mmol) and DPE (0.525 mmol) were mixed in THF (8.51 mL) at −78 °C and the reaction mixture was allowed to stir for 0.5 h at −78 °C. Then, the deep red colored solution was slowly added in a titration manner to the in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) (M_n = 10 600 g/mol, PS/P(F_8H_2−MA) = 54/46 (*w*/*w*), 0.120 mmol for BnBr function) in THF (20.7 mL) at −78 °C. The addition was stopped when the red color remained even after 1 h. The reaction mixture was then allowed to stir at −78 °C for 24 h. After quenching the reaction with degassed methanol, the polymer solution was poured into a large amount of methanol to precipitate the polymers. By comparing the SEC peak areas, the polymer yield was estimated. The target 4-arm A_2B_2 star-branched polymers were obtained in 47 and 100% yields, respectively, with the use of in-chain-BnBr-functionalized block copolymers having M_n values of 21 700 g/mol and 10 600 g/mol. These star-branched polymers were isolated by SEC fractionation and freeze-dried twice from their absolute benzene solutions. M_n = 23 600 g/mol and 43 500 g/mol (RALLS), M_w/M_n = 1.09 and 1.09 (SEC). ^{1}H NMR ($CDCl_3$) (300 MHz): δ = 7.04−6.50 (broad, aromatics), 4.25 (s, −O−CH_2−CH_2−), 2.45 (s, −O−CH_2−CH_2−), 2.21−0.73 (broad, backbone chains), 1.09 (s, C−CH_3).

Results and Discussion

We previously reported that typical perfluorinated methacrylate monomers such as 2,2,2-trifluoroethyl methacrylate (F_1M_1−MA) and 2-(perfluorobutyl)ethyl methacrylate (F_4H_2−MA) undergo living anionic polymerization in THF at −78 °C.[51,64,65] The resulting polymers were observed to possess predictable molecular weights (9000−21 000 g/mol) and narrow molecular weight distributions (M_w/M_n ~ 1.1 or smaller). Although F_8H_2−MA was also readily and quantitatively polymerized under the same conditions, the resulting polymers were always precipitated completely during the course of the polymerization. They were

Scheme 1. Synthesis of 3-Arm ABC Miktoarm Star-Branched Polymers Using Soluble in-Chain-BnBr-Functionalized PS-*block*-P(F_8H_2−MA)



practically insoluble in most organic solvents such as benzene, chloroform, dichloromethane, ethyl acetate, acetone, THF, 1,4-dioxane, DMF, DMSO, and hot toluene and the characterizations by SEC, RALLS, and ^{1}H NMR could be no longer performed.

On the other hand, the sequential block polymerization of styrene, after end-capping with DPE, followed by F_8H_2−MA, proceeded homogeneously to quantitatively afford a THF-soluble diblock copolymer, PS-*bloc*k-P(F_8H_2−MA), with predictable molecular weight and composition and a narrow molecular weight distribution (M_n = 18 000 g/mol, PS/P(F_8H_2−MA) = 53/47 (*w*/*w*), and M_w/M_n = 1.06). This result clearly indicates that F_8H_2−MA similar to F_1H_1−MA and F_4H_2−MA undergoes living anionic polymerization. We also observed that block copolymers having P(F_8H_2−MA) segments of around or less than 50 wt % were soluble in THF, but became insoluble with increasing the content of P(F_8H_2−MA) segment.

Since the synthetic difficulty of FL star-branched polymers is attributed to the insolubility of P(F_8H_2−MA) segment as often mentioned, the presence of THF-soluble block copolymer, PS-*block*-P(F_8H_2−MA), prompts us to utilize as the soluble building block to synthesize star-branched polymers consisting of P(F_8H_2−MA) segments. Thus, we have herein proposed a novel methodology using THF-soluble block copolymers as key building blocks in the synthesis of miktoarm star-branched polymers consisting of P(F_8H_2−MA) segments. For this synthesis, a new diblock copolymer, PS-*block*-P(F_8H_2−MA), in-chain-functionalized with 3-*tert*-butyldimethylsilyloxymethylphenyl (SiOMP) group between the two blocks was prepared. This block copolymer is designed to solubilize P(F_8H_2−MA) segment during the star-branched polymer synthesis and to introduce the P(F_8H_2−MA) segment into the target star-branched polymer. Furthermore, the in-chain-SiOMP group is designed to be transformed into a highly reactive benzyl bromide (BnBr) function that can smoothly undergo coupling reaction to introduce other arm segments into stars.

As illustrated in Scheme 1, three reaction steps are basically employed in the proposed methodology in order to synthesize a variety of miktoarm star-branched polymers consisting of P(F_8H_2−MA) segments. The first reaction step is to prepare the in-chain-SiOMP-functionalized PS-*block*-P(F_8H_2−MA) by the living anionic polymerization, in which styrene, 1-(3-*tert*-butyldimethylsilyloxymethylphenyl)-1-phenylethylene (**1**), and F_8H_2−MA are sequentially polymerized with *sec*-BuLi in THF at −78 °C. The SiOMP-functionalized DPE, **1**, was used to introduce a SiOMP group at the living chain-end of PS. A 3-fold or more excess of LiCl was added prior to the polymerization of F_8H_2−MA to narrow the molecular weight distribution of the resulting P(F_8H_2−MA) segment. As expected, the polymerization proceeded homogeneously to quantitatively afford the objective in-chain-SiOMP-functionalized PS-*block*-P(F_8H_2−MA). The second reaction step is to transform the SiOMP group into BnBr function by treatment with a 1:1 mixture of $(CH_3)_3SiCl$ and LiBr. The completion of the transformation reaction was confirmed by the disappearance of methyl protons of the SiOMP group as well as benzyl methylene protons of the benzyl silyl ether. In the third reaction step, the in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) thus prepared is reacted with another living anionic polymer prepared in advance to introduce the arm segment. It should be mentioned that the use of THF-soluble in-chain-SiOMP (or -BnBr) -functionalized PS-*block*-P-(F_8H_2−MA) enables the second and third reaction steps to smoothly and quantitatively proceed.

Synthesis of 3-Arm ABC Miktoarm Star-Branched Polymers. Unless otherwise stated, the molecular weight of arm segment is adjusted to be around 10 000−12 000 g/mol to keep the molecular weight factor constant. As illustrated in Scheme 1, a new 3-arm ABC miktoarm star-branched polymer was synthesized by the coupling reaction of an in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) (M_n = 25 000 g/mol and PS/P(F_8H_2) = 52/48 (w/w)) with a 2.0-fold excess of living poly(2-vinylpyridine) (P2VP) (M_n = 10 800 g/mol) in THF at −40 °C for 24 h. The red color of living P2VP remained during the reaction, indicating that C−F bonds of the monomer and the polymer are stable toward the living P2VP chain-end anion under such conditions. As shown in Figure 1, the SEC profile of the crude reaction mixture exhibits only two distinct sharp peaks corresponding to the target 3-arm star and the deactivated P2VP used in excess in the coupling reaction. By comparing the peak areas, the reaction was estimated to be quantitative. The 3-arm ABC star-branched polymer was isolated in 80% yield by fractionation. The isolated polymer exhibited a narrow monomodal SEC distribution (M_w/M_n = 1.07) (see also Figure 1) and possessed predictable molecular weight and composition, as listed in Table 1. These results clearly demonstrated the successful synthesis of a 3-arm ABC miktoarm star-branched polymer composed of PS, P(F_8H_2−MA), and P2VP segments.

Similarly, another 3-arm ABC star-branched polymer was synthesized by the coupling reaction of the same in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) with a 2-fold excess of living poly(methyl methacrylate) (PMMA) under the identical conditions mentioned above. The reaction also quantitatively proceeded to afford the expected and the well-defined 3-arm ABC star composed of PS, P(F_8H_2−MA), and PMMA segments (see also Table 1). Thus, obviously, the P(F_8H_2−MA) segment which is insoluble in THF could be readily introduced by using a THF-soluble AB diblock copolymer, PS-*block*-P(F_8H_2−MA). Figure 2 shows ^{1}H NMR spectra of both 3-arm ABC miktoarm star-branched polymers. The rational integration of the characteristic peaks clearly observed at 7.2−6.4, 4.25, 8.4−8.1, and 3.62 ppm corresponding to phenyl protons of PS, methylene protons of P(F_8H_2−MA), −N=CH− proton of P2VP, and methoxy protons of PMMA, indicating the successful insertion of the desired segments into the target star with the expected composition.

As a control experiment, the coupling reaction of in-chain-BnBr-functionalized PS-*block*-PMMA with a 2-fold excess of living P(F_8H_2−MA) was carried out under the same conditions in THF at −40 °C for 24 h. Because of the insolubility of living P(F_8H_2−MA) in THF, the reaction system was heterogeneous. As expected, no coupling reaction practically occurred and both the starting in-chain-BnBr-functionalized PS-*block*-PMMA and the homopolymer of F_8H_2−MA were recovered nearly quantitatively from the solution and precipitate, respectively. Thus, obviously, the proposed methodology using in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) as a THF-soluble building block is very effective to synthesize miktoarm star-branched polymers consisting of P(F_8H_2−MA) segments which are originally insoluble in THF.

Synthesis of 4-Arm A_3B and ABC_2 Miktoarm Star-Branched Polymers. For the synthesis of 4-arm star-branched polymers, a THF-soluble in-chain-(SiOMP)$_2$-functionalized PS-*block*-P(F_8H_2−MA) was newly prepared as another building block by the living anionic polymerization where styrene, 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenylethylene) (**2**), and F_8H_2−MA were sequentially polymerized with *sec*-BuLi as an initiator. The functionalized DPE derivative, **2**, was used instead of **1** to introduce two SiOMP groups. The resulting in-chain-functionalized diblock copolymer was treated with $(CH_3)_3SiCl$-LiBr to transform the two SiOMP groups into two BnBr functions and, which in turn was used to react with another living anionic polymer in a manner similar to the synthesis of 3-arm star-branched polymers. The synthetic outline is shown in Scheme 2. Needless to say, both in-chain-(SiOMP)$_2$ and -(BnBr)$_2$-functionalized diblock copolymers were soluble in THF and the coupling reactions herein carried out all proceeded homogeneously.

Typically, a 4-arm A_3B miktoarm star-branched polymer was synthesized by the coupling reaction of the in-chain-(BnBr)$_2$-functionalized PS-*block*-P(F_8H_2−MA) with living PS end-capped with DPE in THF at −40 °C for 24 h. A 2-fold excess of living PS was used toward each BnBr function. The reaction was observed to proceed cleanly and quantitatively and this was confirmed by the SEC analysis which exhibited only two distinct peaks with expected peak areas. The results are summarized in Table 2. As can be seen, the M_n value calculated (42 200 g/mol) is in good agreement with those determined (40 400 and 40 900 g/mol) by ^{1}H NMR and RALLS. A narrow molecular weight distribution was attained. Moreover, the composition observed by ^{1}H NMR was consistent with that calculated from the monomer feed ratio. Thus, the successful synthesis of 4-arm A_3B star composed of one P(F_8H_2−MA) and three PS segments was confirmed by these characterization results.

Likewise, two new 4-arm ABC_2 miktoarm star-branched polymers could also be synthesized by the coupling reaction of the same in-chain-(BnBr)$_2$-functionalized PS-*block*-P(F_8H_2−MA) with either living P2VP or PMMA under the same conditions. Their characterization results are also listed in Table 2. All of the coupling reactions were observed to proceed homogeneously during the reaction. The SEC profiles of the resulting crude polymer mixtures exhibited only the expected two peaks corresponding to the objective star and the deactivated living polymer used in excess in both cases.

Thus, the effectiveness utilizing of the in-chain-(BnBr)$_2$-functionalized PS-*block*-P(F_8H_2−MA) as a THF-soluble

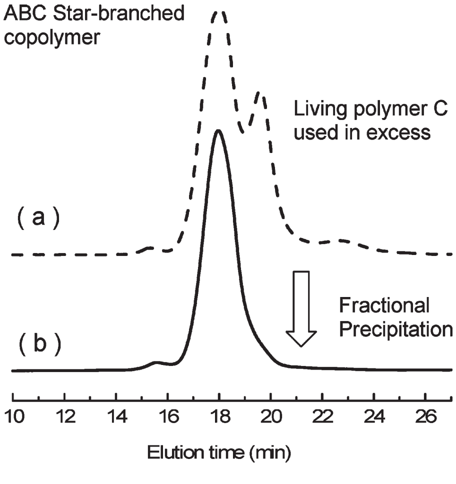


Figure 1. SEC profiles of ABC miktoarm star-branched polymers obtained (a) before and (b) after fractional precipitation.

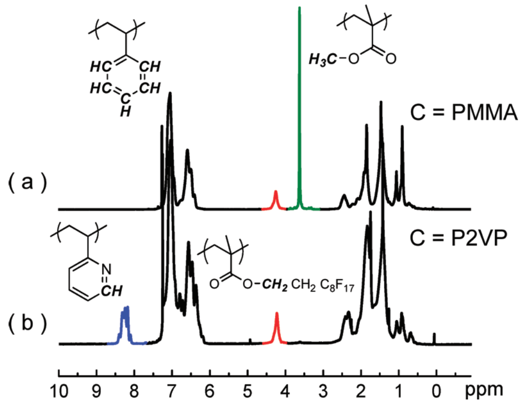


Figure 2. ^{1}H NMR spectra of 3-arm ABC miktoarm star-branched polymers: (a) ABC star composed of PS, P(F_8H_2−MA), and PMMA and (b) ABC star composed of PS, P(F_8H_2−MA), and P2VP.

Table 1. Synthesis of 3-Arm ABC Miktoarm Star-Branched Polymers

		$M_n \times 10^{-3}$ (g/mol)				composition (*w*/*w*)	
polymer	monomer (C)	calcd	NMR[a]	RALLS[b]	M_w/M_n[b]	calcd	obsd[a]
AB−BnBr		23.4	24.5	25.8	1.06	52/48	53/47
ABC	2VP	35.7	34.8	33.3	1.07	35/33/32	37/33/30
ABC	MMA	34.2	33.4	35.3	1.06	36/34/30	38/34/28

[a] Determined by ^{1}H NMR. [b] Determined by SEC equipped with triple detectors.

Scheme 2. Synthesis of 4-Arm Miktoarm Star-Branched Polymers Using THF Soluble in-Chain-$(BnBr)_2$-Functionalized PS-*block*-P(F_8H_2−MA)

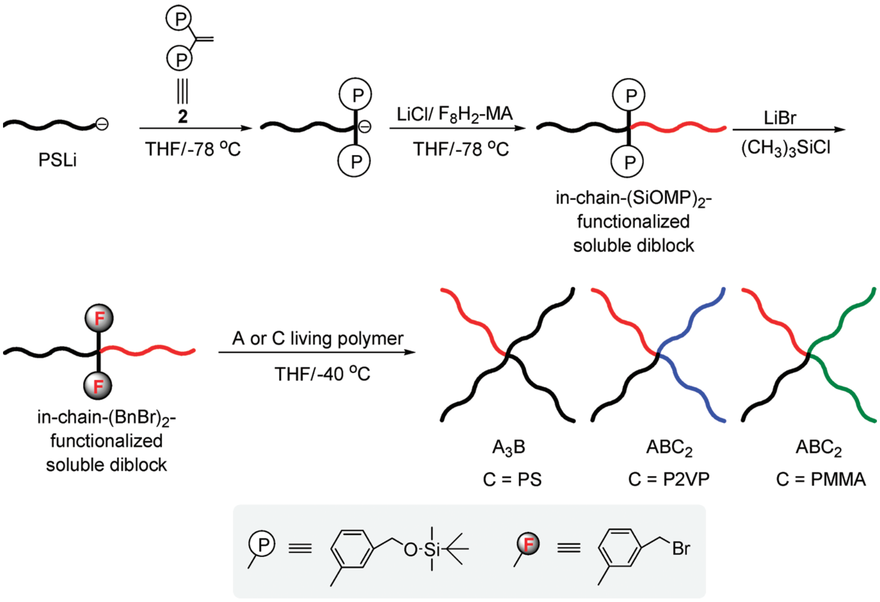


Table 2. Synthesis of 4-Arm Miktoarm Star-Branched Polymers

polymer	monomer (C)	$M_n \times 10^{-3}$ (g/mol) calcd	NMR[a]	RALLS[b]	M_w/M_n[b]	composition (w/w) calcd	obsd[a]
AB−$(BnBr)_2$		24.2	23.9	26.3	1.06	51/49	52/48
A_3B	St	42.2	40.4	40.9	1.08	87/13	89/11
ABC_2	2VP	51.5	52.1	52.2	1.07	27/26/47	24/22/54
ABC_2	MMA	41.5	42.7	42.8	1.04	25/24/51	29/27/44

[a] Determined by ^{1}H NMR. [b] Determined by SEC equipped with triple detectors.

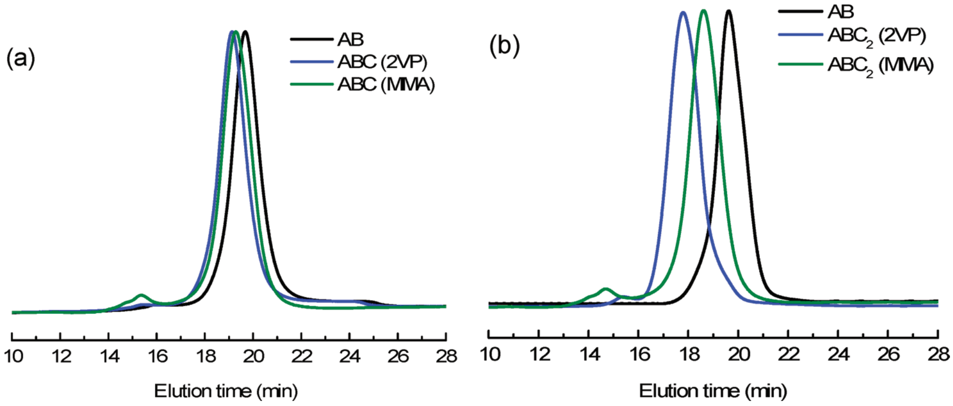
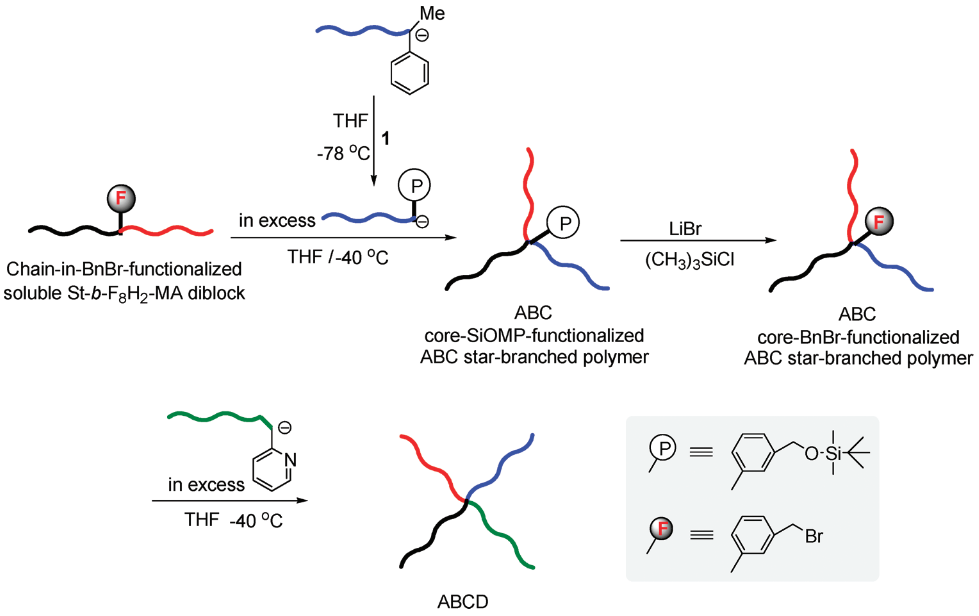


Figure 3. SEC profiles of 3-arm ABC and 4-arm ABC_2 miktoarm star-branched polymers.

building block obviously enables a variety of 4-arm miktoarm star-branched polymers consisting of THF-insoluble P(F_8H_2−MA) segments to be synthesized without any difficulty. Finally, SEC profiles of 3-arm ABC and 4-arm ABC_2 miktoarm star-branched polymers are shown in Figure 3.

Synthesis of 4-Arm ABCD Miktoarm Star-Branched Polymer. In order to demonstrate a more versatility of the proposed methodology, the synthesis of a 4-arm ABCD star-branched polymer was carried out by using in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA). The synthetic outline is illustrated in Scheme 3. At first, an in-chain-SiOMP-functionalized PS-*block*-P(F_8H_2−MA) was prepared and treated with $(CH_3)_3SiCl$-LiBr to transform the SiOMP group into BnBr function. Then, the resulting in-chain-BnBr-functionalized diblock copolymer was exposed to excess of the living poly(α-methylstyrene) (PαMS) functionalized with SiOMP terminus which was polymerized with *sec*-BuLi and end-capped with **1**. The coupling reaction efficiently proceeded to afford a 3-arm ABC star-branched polymer core-functionalized with SiOMP group. The resulting 3-arm star was again treated with $(CH_3)_3SiCl$-LiBr to transform the SiOMP group into BnBr function at the core. Finally, the core-BnBr-functionalized 3-arm ABC star thus prepared was coupled with living P2VP in THF at −40 °C for 24 h. The SEC profiles of 3-arm ABC and 4-arm ABCD stars obtained by the first and second coupling reactions, followed by fractionation, are shown in Figure 4. The peak of the target ABCD star was slightly shifted to a higher molecular weight side from that of the ABC star. A small amount of a lower molecular tailing (≤8%) may correspond to the unreacted AB diblock copolymer or the dimeric product

Scheme 3. Synthesis of 4-Arm ABCD Miktoarm Star-Branched Polymer Composed of PS, P(F_8H_2−MA), PαMS, and P2VP Segments Using THF-Soluble in-Chain-BnBr-Functionalized PS-*block*- P(F_8H_2−MA)



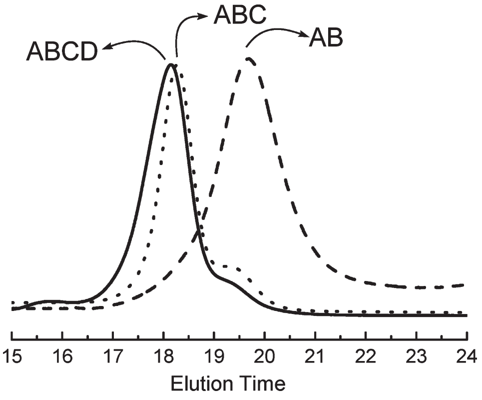


Figure 4. SEC profiles of AB building block, 3-arm ABC, and 4-arm ABCD miktoarm star-branched polymers after fractional precipitation.

of living PαMS which is often formed by allowing living PαMS to stand for a long time like 24 h.

After removing the lower molecular weight polymer by SEC fractionation, the isolated polymer was characterized by SEC, RALLS, and ^{1}H NMR, as summarized in Table 3. The expected and well-defined structures of the 4-arm ABCD star-branched polymer were confirmed by good agreement between the M_n value calculated and that determined by ^{1}H NMR or RALLS and the narrow molecular weight distribution. Furthermore, the ^{1}H NMR of the resulting polymer showed the distinguished peaks for four polymer segments with rational peak areas close to those calculated from feed ratios. Thus, both 3-arm ABC and 4-arm ABCD miktoarm star-branched polymers were successfully synthesized by using in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA).

Synthesis of 4-Arm A_2B_2 Miktoarm Star-Branched Polymer Composed of Two PS and Two P(F_8H_2−MA) Segments. Since it is difficult to synthesize the star-branched polymers possessing two P(F_8H_2−MA) segments by the methodologies developed in the preceding sections, the coupling reaction of in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) with a dianionic agent is newly proposed, as illustrated in Scheme 4. With this reaction, a 4-arm star-branched polymer of the A_2B_2 type having two P(F_8H_2−MA) segments could be synthesized. As the dianionic coupling agent, 1,4-dilithio-1,1,4,4-tetraphenylbutane (**3**) was prepared by the reaction of lithium naphthalenide with a 3.1-fold excess of DPE in THF at −78 °C for 0.5 h and then *in situ* reacted with in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) (M_n = 21 700 g/mol and PS/P(F_8H_2−MA) = 53/47 (w/w)) in a titration manner under the conditions in THF at −78 °C. The deep red color of **3** disappeared immediately on mixing with the in-chain-BnBr-functionalized block copolymer at the early stage of the reaction, but faded gradually with time. The addition of **3** was stopped when a red color was observed to remain and the reaction mixture was allowed to stand at −78 °C for 24 h. Finally, the reaction was quenched with degassed methanol and the polymers were precipitated in methanol. The SEC profile of the crude reaction mixture exhibited almost comparable two peaks corresponding to the coupled 4-arm A_2B_2 star and the starting AB diblock copolymer (or one-side coupled product). The yield of the 4-arm A_2B_2 star-branched polymer was estimated to be 47% based on the peak area.

On the other hand, a nearly 100% yield was obtained by coupling **3** with a lower molecular weight in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA) (M_n = 10 600 g/mol and PS/P(F_8H_2−MA) = 54/46 (w/w)) in a similar manner, as shown in Figure 5.

The polymer isolated only by precipitation in methanol was found to be 23 600 g/mol in M_n value which was in agreement with that calculated (M_n = 21 200 g/mol) and possess a narrow molecular weight distribution (M_w/M_n = 1.09). The composition (54/46) observed by ^{1}H NMR was consistent with the calculated value (54/46). These results clearly indicate that the coupling reaction was complete to give the target 4-arm A_2B_2 miktoarm star-branched polymer quantitatively. Thus, the efficiency of the coupling reaction is significantly influenced by the molecular weight of in-chain-BnBr-functionalized PS-*block*-P(F_8H_2−MA). This may possibly be attributed to the steric hindrance between the one-side coupled product having DPE-derived anion and the in-chain-BnBr-functionalized block copolymer. Using different

Table 3. Synthesis of 3-Arm ABC and 4-Arm ABCD Miktoarm Star-Branched Polymers

		$M_n \times 10^{-3}$ (g/mol)				composition (w/w)	
polymer	monomers (C, D)	calcd	NMR[a]	RALLS[b]	M_w/M_n[b]	calcd	obsd[a]
AB-BnBr		23.4	24.5	25.8	1.06	52/48	53/47
ABC	α-MS	39.3	38.7	36.3	1.08	33/31/36	33/29/38
ABCD	2VP	46.7	49.1	46.8	1.08	25/23/27/25	25/22/29/24

[a] Determined by ^{1}H NMR. [b] Determined by SEC equipped with triple detectors.

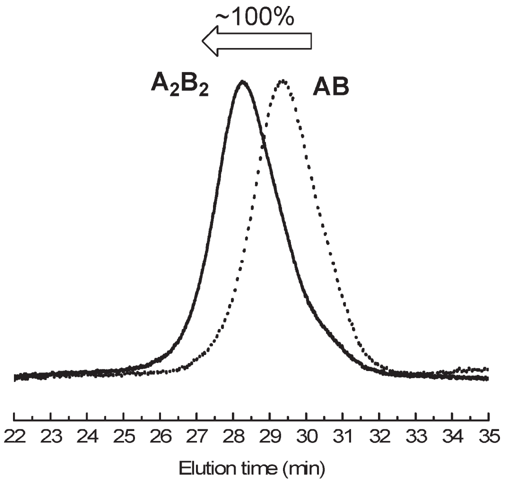
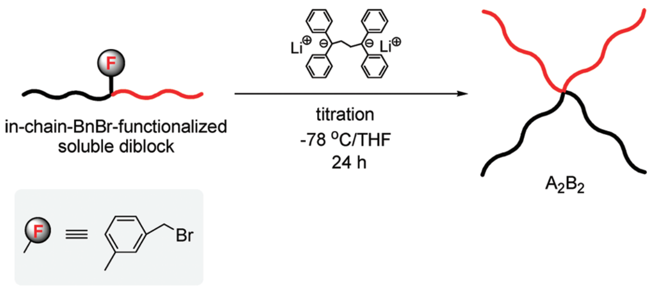


Figure 5. SEC profiles of in-chain-BnBr-functionalized AB diblock copolymer and 4-arm A_2B_2 miktoarm star-branched polymer.

Scheme 4. Synthesis of 4-Arm A_2B_2 Miktoarm Star-Branched Polymers



dianionic coupling agents and optimization of the reaction conditions will be needed in this coupling reaction.

Conclusions

We have herein proposed and developed a novel methodology based on a new concept, in which a THF-soluble in-chain-$(BnBr)_n$-functionalized PS-*block*-P(F_8H_2−MA) (n = 1 or 2) is used as a key building block in the synthesis of star-branched polymers consisting of P(F_8H_2−MA) arm segment(s) which is originally insoluble in most organic solvents including THF. With this methodology, we have successfully synthesized a variety of 3-arm ABC and 4-arm A_3B, ABC_2, ABCD, and A_2B_2 miktoarm star-branched polymers consisting of P(F_8H_2−MA) arm segment(s). The resulting stars were observed to be all well-defined in star-branched architecture and precisely controlled in arm segment because all arm segments were prepared by living anionic polymerization of the corresponding monomers. It should be mentioned that the synthesis of well-defined three and four compositional miktoarm star-branched polymers such as ABC, ABC_2, and ABCD types is still difficult even at the present time and only a limited number of successful examples has been reported so far.

The methodology herein proposed satisfactorily works and opens a new and general route for the synthesis of miktoarm star-branched polymers consisting of insoluble arm segment(s), which are difficult to be synthesized by using insoluble arm precursors. The synthetic studies of star-branched polymers by using in-chain-functionalized diblock copolymers composed of PS and either P(F_mH_n−MA) ($m \geq 9$) or poly(4-vinylpyridine) segment is now in progress.

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