Synthesis of Novel Multifunctional Polyisobutylenes at Chain End(s) and Their Application to A_nB Asymmetric Star and A_nBA_n Pompom Polymers by Combination of Living Cationic and Anionic Polymerizations

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ABSTRACT: The synthesis of an array of ω- or α,ω-multifunctional polyisobutylenes (PIBs) with 2, 4, and 8 benzyl bromide moieties has been demonstrated by an iterative divergent methodology using ω- or α,ω-functional PIBs with allyl halide moiety (moieties) as starting materials. The multifunctional PIBs were successfully applied for the synthesis of A_2B, A_4B, and A_8B asymmetric star polymers as well as A_2BA_2, A_4BA_4, and A_8BA_8 pompom polymers where A and B were poly(methyl methacrylate) (PMMA) and PIB segments, respectively. The synthetic method involved the coupling reaction of living PMMA with multifunctional PIBs in tetrahydrofuran at −40 °C. The coupling efficiencies were virtually quantitative in all cases. The well-defined structures of the resulting branched polymers were confirmed by size exclusion chromatography−right angle laser light scattering and ^{1}H NMR analyses. The microphase-separated morphologies of all A_nBA_n type pompom polymers were supported by differential scanning calorimetry. The stress−strain plots of solution-cast films of A_nBA_n type pompom polymers showed good elastomeric properties (279−444% elongations at break and 12.6−20.7 MPa tensile strengths).

Introduction

There has been a growing interest in chain-end functional polymers with well-defined structures. Functional polymers can be utilized, for instance, in chain extension, branching, or cross-linking reactions with multifunctional reagents, coupling and linking with reactive groups on the other oligomer or polymer chains, and as macroinitiators in the polymerization of other monomers. Many studies on chain-end functional polystyrenes and poly(1,3-diene)s based on living anionic polymerization have so far been reported.[1] In the area of living cationic polymerization, there have been also many examples of synthetic methodologies especially for chain-end functional polyisobutylenes (PIB)s.[2] Well-characterized and quantitatively functional PIBs with a wide variety of termini are currently available, including hydroxy,[3] amino,[4] epoxy,[3] methacryloyl,[5] maleic anhydride,[6] allyl,[7] and allyl halides.[8,9] In most cases, the number of functional groups is one or two at an ω-chain end or α,ω-chain ends, respectively. Although it is possible to introduce more than three functional groups via a star-branched structure,[3] examples of functionalization with two or more groups per terminus are rare. To the best of our knowledge, there is only one example of ω-functional PIB with two maleic anhydride moieties in the field of carbocationic polymerization.[6]

In the past decade, Hirao and co-workers have been developing new methodologies for introducing a definite number of multiple benzyl halide moieties per terminus at an ω-chain end, α,ω-chain ends, or within the polymer chain by using specially designed 1,1-diphenylethylene derivatives based on living anionic polymerization.[10] The most promising method to multiply benzyl halide moieties involves an iterative divergent approach in which only two sets of the reactions are required for the entire iterative reaction sequence: (1) a coupling reaction of the terminal benzyl bromide moiety(moieties) with the functional 1,1-diphenylalkyl anion to introduce double 3-*tert*-butyldimethylsilyloxymethylphenyl groups at polymer chain end(s) and (2) a transformation reaction into benzyl halide moieties.[11] By repeating this reaction sequence, quantitatively chain-end functional polystyrenes with 2, 4, 8, 16, 32, and 64 benzyl bromide moieties were synthesized without difficulty.

Recently, Faust and co-workers discovered the synthetic method for ω- and α,ω-functional PIBs with allyl halide moiety (moieties) by reacting 1,3-butadiene with living cationic PIB initiated with 2-chloro-2,4,4-trimethylpentane or 5-*tert*-butyl-1,3-bis(1-chloro-1-methylethyl)benzene, followed by an instantaneous ion collapse.[8,9] The proposed direct method without protection/deprotection processes is highly advantageous. By applying the aforementioned iterative divergent approach here, novel chain-end multifunctional PIBs with a definite number of n^2 benzyl halide moieties can be synthesized starting from allyl halide functional PIBs. Benzyl halide moieties introduced at the PIB chain end(s) can be easily converted to a wide variety of other functional groups including hydroxy, amino, carboxy, vinyl, (meth)acryloyl, azide, alkyne, mercapto, and so on. In addition, the functional PIBs can participate in building blocks of branched polymers by coupling reactions with other functional polymers or living polymers. The initiation of a living radical polymerization from multiple benzyl bromide groups at the chain end(s) is also possible. Thus, functional PIBs offer the potential of providing an extensive library of branched polymers with different blocks by selecting a combination of segments. In particular, branched polymers with heterophase structures such as asymmetric star polymers and pompom polymers have attracted much attention not only from a synthetic viewpoint but also from an expectation that they would exhibit

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unique physical and reological properties unlike their linear counterparts.[12]

Herein we report the first synthesis of a series of ω- and α,ω-functional PIBs with 2, 4, and 8 benzyl bromide (BnBr) moieties per terminus (series 1: PIB(BnBr)$_2$, PIB(BnBr)$_4$, and PIB(BnBr)$_8$; series 2: (BnBr)$_2$PIB(BnBr)$_2$, (BnBr)$_4$PIB(BnBr)$_4$, and (BnBr)$_8$PIB(BnBr)$_8$) based on the iterative divergent methodology using ω- and α,ω-functional PIBs with allyl halide moiety (moieties) as starting materials. New two-component branched polymers, asymmetric star polymers (series 3: A_2B, A_4B, and A_8B) and pompom polymers (series 4: A_2BA_2, A_4BA_4, and A_8BA_8), were also synthesized by coupling the functional PIBs with living anionic polymers of methyl methacrylate by combining living cationic and anionic polymerizations. The proposed methodology would be useful from the viewpoint that it provides a facile route to link different polymer segments together obtained by other polymerization techniques. Although Hirao's group has already published many examples of asymmetric star and pompom polymers by basically the same methodology,[10,11] it is still a challenge to extend the proposed methodology for the synthesis of the above-mentioned branched polymers with new combination of polymer segments.

Experimental Section

Materials. All reagents were purchased from Sigma-Aldrich Corp. (>99%) unless otherwise stated. Tetrahydrofuran (THF, 99%, Mitsubishi Chemical Co., Ltd.) was refluxed over sodium wire for 6 h, distilled from lithium aluminum hydride under nitrogen, and finally distilled from its sodium naphthalenide solution on a vacuum line. Benzene (99%) was washed with concentrated sulfuric acid twice, water once, 5% aqueous sodium hydroxide (NaOH) twice, and then water twice. It was predried over calcium chloride and then over phosphorus pentoxide. Finally, it was distilled from 1,1-diphenylhexyllithium (DPHLi). *sec*-Butyllithium (^{s}BuLi, 1.3 M in cyclohexane) was used after diluting with dried heptane distilled from DPHLi. Methyl methacrylate (MMA, 98%) was washed with 5% aqueous NaOH and water. After drying over magnesium sulfate, it was filtered, distilled from calcium hydride (CaH$_2$), and finally distilled from trioctylaluminum (ca. 2 mol %) on the vacuum line. 1,1-Diphenylethylene (DPE) was distilled from CaH$_2$ under reduced pressure and then distilled from its DPHLi solution on a vacuum line. Chloroform, acetonitrile, and bromotrimethylsilane (TMS-Br, 95%, Tokyo Chemical Inductry Co. Ltd.) were distilled from CaH$_2$ under nitrogen. Lithium chloride (LiCl, 99%) was dried under a high vacuum (10^{-6} Torr) at 100 °C for 12 h. 1,1-Bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**)[13] and ω-functional PIB with one allyl chloride moiety (PIB(AllylCl)$_1$) and α,ω-functional PIB with allyl chloride moieties ((AllylCl)$_1$PIB(AllylCl)$_1$)[8] were synthesized as described elsewhere.

Synthesis of ω-Functional Polyisobutylenes with 2, 4, and 8 Benzyl Bromide Moieties. All reactions using the functional 1,1-diphenylalkyl anion obtained from 1:1 reaction of **1** and ^{s}BuLi were carried out in sealed reactors equipped with break-seals under high vacuum conditions (10^{-6} Torr). The functionalized 1,1-diphenylalkyl anion prepared from **1** (0.754 mmol) in THF (3.94 mL) and ^{s}BuLi (0.540 mmol) in heptane (3.31 mL) was added to a THF solution (23.7 mL) of PIB(AllylCl)$_1$ (M_n = 5820, PDI = 1.06, 1.70 g, 0.292 mmol) at −78 °C. The reaction mixture was stirred for 30 min. Then, the reaction was terminated with degassed methanol (5 mL). After THF was evaporated, the resulting polymer was purified by reprecipitation using a hexanes/methanol system twice and azeotropic distillation from its absolute benzene solution twice to afford ω-functional PIB with two 3-*tert*-butyldimethylsilyloxymethylphenyl (SMP) groups, PIB(SMP)$_2$ (1.71 g, 93%). PIB(SMP)$_2$ (1.62 g, 0.516 mmol for SMP groups) and TMS-Br (3.90 g, 25.5 mmol) were dissolved in a mixture of chloroform (45 mL) and acetonitrile (15 mL). The solution was heated to 40 °C and allowed to stand for 24 h. The solution was washed with water three times to remove a large excess of LiBr. The organic layer was concentrated under reduced pressure, followed by reprecipitation using a hexanes/methanol system twice. It was dried by azeotropic distillation from its absolute benzene solution twice to afford PIB(BnBr)$_2$ (1.43 g, 90%). ^{1}H NMR: δ 0.60−0.92 ppm (m, 6 H, −CH(CH_3)CH$_2$CH_3), 0.92−1.18 ppm (m, −CH$_3$ in the PIB main chain), 1.22−1.32 ppm (m, −CH$_2$− in the PIB main chain), 4.35 ppm (s, 4H, −CH$_2$Br), 4.78 and 5.23 ppm (m, 2H, −C*H*═C*H*−), and 6.98−7.17 ppm (m, 8H, Ar).

PIB(BnBr)$_4$ and PIB(BnBr)$_8$ were synthesized in a similar manner. The functional 1,1-diphenylalkyl anion was always used in 2-fold excess toward benzyl bromide moieties in the coupling reaction with PIB(BnBr)$_n$. *PIB(BnBr)$_4$*: ^{1}H NMR: δ 0.61−0.92 ppm (m, 18 H, −CH(CH_3)CH$_2$CH_3), 0.92−1.20 ppm (m, −CH$_3$ in the PIB main chain), 1.22−1.33 ppm (m, −CH$_2$− in the PIB main chain), 4.35 ppm (s, 8H, −CH$_2$Br), 4.79 and 5.20 ppm (m, 2H, −C*H*═C*H*−), and 6.96−7.18 ppm (m, 24H, Ar). *PIB(BnBr)$_8$*: ^{1}H NMR: δ 0.77−0.99 ppm (m, 42 H, −CH(CH_3)CH$_2$CH_3), 0.99−1.19 ppm (m, −CH$_3$ in the PIB main chain), 1.29−1.43 ppm (m, −CH$_2$− in the PIB main chain), 6.74−7.13 ppm (m, 12H, −(Ar)$_2$CCH_2Ar−), 4.35 ppm (s, 16H, −CH$_2$Br), 4.80 and 5.20 ppm (m, 2H, −C*H*═C*H*−), and 6.96−7.20 ppm (m, 56H, Ar).

Synthesis of α,ω-Functional Polyisobutylenes with 2, 4, and 8 Benzyl Bromide Moieties. All reactions using the functional 1,1-diphenylalkyl anion obtained from 1:1 reaction of **1** and ^{s}BuLi were carried out in sealed reactors equipped with break-seals under high-vacuum conditions (10^{-6} Torr). The functional 1,1-diphenylalkyl anion prepared from **1** (0.605 mmol) in THF (3.20 mL) and ^{s}BuLi (0.397 mmol) in heptane (4.64 mL) was added to (AllylCl)$_1$PIB(AllylCl)$_1$ (M_n = 35 200, PDI = 1.04, 2.77 g, 0.0787 mmol) dissolved in a mixture of THF (28.7 mL) and heptane (12.1 mL) at −78 °C. The reaction mixture was stirred for 30 min. Then, the reaction was terminated with degassed methanol (5 mL). After THF was evaporated, the resulting polymer was reprecipitated using a hexanes/methanol system twice and azeotropically distilled from its absolute toluene solution twice to afford (SMP)$_2$PIB(SMP)$_2$ (2.47 g, 87%). (SMP)$_2$PIB(SMP)$_2$ (2.47 g, 0.273 mmol for SMP groups) and TMS-Br (2.15 g, 14.0 mmol) were dissolved in a mixture of chloroform (75 mL) and acetonitrile (18 mL). The solution was heated to 40 °C and allowed to stand for 24 h. The solution was washed with water three times to remove a large excess of LiBr. The organic layer was concentrated under reduced pressure, followed by reprecipitation using a hexanes/methanol system twice. It was dried by azeotropic distillation from its absolute benzene solution twice to afford (BnBr)$_2$PIB(BnBr)$_2$ (2.25 g, 92%). ^{1}H NMR: δ 0.60−0.93 ppm (m, 12 H, −CH(CH_3)CH$_2$CH_3), 0.93−1.19 ppm (m, −CH$_3$ in the PIB main chain), 1.19−1.46 ppm (m, −CH$_2$− in the PIB main chain), 4.35 ppm (s, 8H, −CH$_2$Br), 4.78 and 5.28 ppm (m, 4H, −C*H*═C*H*−), and 6.99−7.17 ppm (m, 16H, Ar).

(BnBr)$_4$PIB(BnBr)$_4$ and (BnBr)$_8$PIB(BnBr)$_8$ were synthesized in the similar manner. The functional 1,1-diphenylalkyl anion was always used in 2-fold excess toward benzyl bromide moieties in the coupling reaction with (BnBr)$_n$PIB(BnBr)$_n$. *(BnBr)$_4$PIB(BnBr)$_4$*: ^{1}H NMR: δ 0.61−0.93 ppm (m, 36 H, −CH(CH_3)CH$_2$CH_3), 0.93−1.14 ppm (m, −CH$_3$ in the PIB main chain), 1.14−1.45 ppm (m, −CH$_2$− in the PIB main chain), 4.35 ppm (s, 16H, −CH$_2$Br), 4.78 and 5.28 ppm (m, 4H, −C*H*═C*H*−), and 6.54−7.16 ppm (m, 48H, Ar). *(BnBr)$_8$PIB(BnBr)$_8$*: ^{1}H NMR: δ 0.61−0.93 ppm (m, 84 H, −CH(CH_3)CH$_2$CH_3), 0.93−1.23 ppm (m, −CH$_3$ in the PIB main chain), 1.23−1.45 ppm (m, −CH$_2$− in the PIB main chain), 4.35 ppm (s, 32H, −CH$_2$Br), 4.77 and 5.28 ppm (m, 4H, −C*H*═C*H*−), and 6.34−7.16 ppm (m, 112H, Ar).

Synthesis of A_2B, A_4B, and A_8B Type Asymmetric Star Polymers (A = Poly(methyl methacrylate) and B = Polyisobutylene). A_2B, A_4B, and A_8B type asymmetric star polymers were synthesized by coupling of corresponding PIB(BnBr)$_n$, series 1, with 2.5-fold excess of living PMMA initiated with 1,1-diphenyl-3-methylpentyllithium in the presence of 3-fold excess LiCl. The representative synthetic procedure for the A_2B star polymer is as follows:

DPE (0.352 mmol) in THF (4.33 mL) was added to a heptane (6.71 mL) solution of ^{s}BuLi (0.255 mmol) to prepare the initiator, 1,1-diphenyl-3-methylpentyllithium. After LiCl (0.788 mmol) in THF (3.86 mL) was added, living polymerization of MMA was initiated by adding MMA (2.09 g, 20.9 mmol) in THF (17.1 mL). After 20 min, a THF solution (7.99 mL) of PIB(BnBr)$_2$ (0.302 g, 0.0990 mmol for benzyl bromide moieties) was added to the living PMMA solution in THF at −78 °C. The reaction mixture was then warmed to −40 °C and allowed to stand for an additional 24 h. After terminating the reaction with degassed methanol (5 mL), the reaction mixture was poured into a large amount of methanol (200 mL) to precipitate the polymer followed by freeze-drying from its absolute benzene solution for 24 h (1.16 g, 91%). M_n (SEC-RALLS) = 25 800, PDI = 1.06. ^{1}H NMR: δ 0.60−0.92 ppm (m, $-CH_3$ in the PMMA main chain), 0.92−1.10 ppm (m, $-CH_3$ in the PIB main chain), 1.21−1.42 ppm (m, $-CH_2-$ in the PIB main chain), 1.49−1.99 ppm (m, $-CH_2-$ in the PMMA main chain), 3.44−3.72 ppm (m, $-COOCH_3$ in the PMMA side chain).

A$_4$B star polymer. Isolation yield (1.07 g, 96%). M_n (SEC-RALLS) = 45,400, PDI = 1.03. ^{1}H NMR: δ 0.62−0.90 ppm (m, $-CH_3$ in the PMMA main chain), 0.90−1.09 ppm (m, $-CH_3$ in the PIB main chain), 1.21−1.40 ppm (m, $-CH_2-$ in the PIB main chain), 1.50−2.00 ppm (m, $-CH_2-$ in the PMMA main chain), 3.42−3.72 ppm (m, $-COOCH_3$ in the PMMA side chain).

A$_8$B star polymer. Isolation yield (1.16 g, 94%). M_n (SEC-RALLS) = 123,000, PDI = 1.02. ^{1}H NMR: δ 0.62−0.90 ppm (m, $-CH_3$ in the PMMA main chain), 0.90−1.09 ppm (m, $-CH_3$ in the PIB main chain), 1.21−1.40 ppm (m, $-CH_2-$ in the PIB main chain), 1.55−2.00 ppm (m, $-CH_2-$ in the PMMA main chain), 3.40−3.72 ppm (m, $-COOCH_3$ in the PMMA side chain).

Synthesis of A$_2$BA$_2$, A$_4$BA$_4$, and A$_8$BA$_8$ type Pompom Polymers (*A* = Poly(methyl methacrylate) and *B* = Polyisobutylene). A$_2$BA$_2$, A$_4$BA$_4$, and A$_8$BA$_8$ type pompom polymers were synthesized by coupling of corresponding (BnBr)$_n$PIB(BnBr)$_n$, series 2, with 2-fold excess living PMMA similarly to the asymmetric star polymers. The representative synthetic procedure for the A$_2$BA$_2$ pompom polymer is as follows:

DPE (0.292 mmol) in THF (5.31 mL) was added to a heptane (4.10 mL) solution of ^{s}BuLi (0.241 mmol). After LiCl (0.634 mmol) in THF (4.40 mL) was added, living polymerization of MMA was initiated by adding MMA (0.851 g, 8.51 mmol) in THF (6.45 mL). After 20 min, (BnBr)$_2$PIB(BnBr)$_2$ (1.01 g, 0.113 mmol for benzyl bromide moieties) dissolved in a mixture of THF (15.8 mL) and heptane (2.79 mL) was added to the living PMMA solution at −78 °C. The reaction mixture was stirred at −40 °C for an additional 24 h. After terminating the reaction with degassed methanol (5 mL), the reaction mixture was poured into a large amount of methanol (150 mL) to precipitate the polymer, followed by freeze-drying from its absolute benzene solution for 24 h (1.33 g, 95%). M_n (SEC-RALLS) = 50 200, PDI = 1.02. ^{1}H NMR: δ 0.72−0.90 ppm (m, $-CH_3$ in the PMMA main chain), 0.90−1.20 ppm (m, $-CH_3$ in the PIB main chain), 1.25−1.50 ppm (m, $-CH_2-$ in the PIB main chain), 1.57−2.00 ppm (m, $-CH_2-$ in the PMMA main chain), 3.42−3.82 ppm (m, $-COOCH_3$ in the PMMA side chain).

A$_4$BA$_4$ Pompom Polymer. Isolation yield (0.745 g, 97%). M_n (SEC-RALLS) = 55 000, PDI = 1.02. ^{1}H NMR: δ 0.62−0.90 ppm (m, $-CH_3$ in the PMMA main chain), 0.90−1.23 ppm (m, $-CH_3$ in the PIB main chain), 1.30−1.50 ppm (m, $-CH_2-$ in the PIB main chain), 1.50−2.00 ppm (m, $-CH_2-$ in the PMMA main chain), 3.40−3.72 ppm (m, $-COOCH_3$ in the PMMA side chain).

A$_8$BA$_8$ Pompom Polymer. Isolation yield (0.620 g, 96%). M_n (SEC-RALLS) = 53 100, PDI = 1.03. ^{1}H NMR: δ 0.46−0.90 ppm (m, $-CH_3$ in the PMMA main chain), 0.90−1.13 ppm (m, $-CH_3$ in the PIB main chain), 1.19−1.40 ppm (m, $-CH_2-$ in the PIB main chain), 1.50−2.00 ppm (m, $-CH_2-$ in the PMMA main chain), 3.42−3.70 ppm (m, $-COOCH_3$ in the PMMA side chain).

Measurements. Molecular weights (MWs) and polydispersity indices (PDIs) were measured with a HPLC system equipped with a pump, refractometer (RI), absorbance detector (UV, $\lambda = 254$ nm), online right angle laser light scattering (RALLS) detector ($\lambda = 670$ nm), sample processor, and styragel size exclusion chromatography (SEC) columns connected in the following series: 650, 200, and 75 Å. THF was used as a carrier solvent at a flow rate of 1.0 mL/min at room temperature. MW and PDI data were calculated on the basis of RALLS and RI with the software (omniSEC). The refractive index increment (d*n*/d*c*) was determined for each polymer sample with an Ohtsuka Electronics DRM-1020 refractometer operating at 633 nm (a He−Ne laser). NMR was recorded on a Bruker DPX (300 MHz) in chloroform-*d*. ^{1}H NMR spectra of solutions in chloroform-*d* were calibrated to undeuterated chloroform as internal standard (δ_H 7.23). Chain-end functionalities of SMP groups and BnBr moieties were determined by comparing the ^{1}H NMR signal intensities at 4.79 and 5.20 ppm assigned to the vinylene protons ($-CH{=}CH-$) with those at 0.05 ppm of the silylmethyl protons or at 4.35 ppm of the bromomethylene protons of the polymers, respectively. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu AXMA-CFR mass spectrometer. The spectrometer was equipped with a nitrogen laser (337 nm) and with pulsed ion extraction. The operation was performed at an accelerating potential of 20 kV by linear-positive ion mode. The sample polymer solution (1 g/L) was prepared in THF. The matrix, 1,8-dihydroxy-9(10*H*)-anthracenone (dithranol, Aldrich) (10 mg), and sodium trifluoroacetate (Aldrich) (1 mg) were dissolved in THF (1 mL). The polymer solution (50 μL) was then mixed with a 50 μL of the matrix solution. A 1 μL aliquot of the final solution was deposited onto a sample target plate and dried in air at room temperature. Mass values were calibrated by the three-point method with insulin plus H$^+$ at *m*/*z* 5734.62, insulin β plus H$^+$ at *m*/*z* 3497.96, and α-cyanohydroxycinnamic acid dimer plus H$^+$ at *m*/*z* 379.35. Differential scanning calorimetry (DSC) was performed with a DuPont 2910 differential scanning calorimeter. The glass transition temperatures were taken as the onset point of specific heat jumps. The samples were heated at 20 °C/min under nitrogen, and the second thermograms were recorded. Calibrations were made using indium as a standard. The tensile property was measured on a solution-cast film according to ASTMD638-02a (tensile bar dimensions: width 3.6 mm, gage length 18 mm) at room temperature. Crosshead speed was set at 120 mm/min. The average of four independent experiments was used. All experiments were reproducible within a small error (<5%). The films were prepared by dissolving the polymers in toluene (2.5 wt %), filtering with a Teflon membrane (0.45 μ), and drying very slowly in a Teflon mold for 7 days at room temperature to avoid bubbles in the films, followed by vacuum-drying for 2 days at room temperature. Finally, the films were annealed at 150 °C for 48 h under vacuum. The film thickness was around 0.18 mm.

Results and Discussion

Synthesis of *ω*-Functional Polyisobutylenes with 2, 4, and 8 Benzyl Bromide Moieties (Series 1). A series of *ω*-functional polyisobutylenes with multiple benzyl bromide moieties (PIB(BnBr)$_n$; n = 2, 4, and 8, series 1) was synthesized by the iterative divergent methodology starting from *ω*-functional PIB with one allyl chloride moiety (PIB(AllylCl)$_1$) which was synthesized by the addition reaction of 1,3-butadiene to living PIB cation, followed by instantaneous ion collapse.[8] The synthetic outline is illustrated in Scheme 1. At first, the coupling reaction of PIB(AllylCl)$_1$ (M_n = 5820, PDI = 1.06) with the functional 1,1-diphenylalkyl anion from **1** and ^{s}BuLi and the subsequent transformation reaction with TMS-Br were carried out in THF at −78 °C and in chloroform/acetonitrile (3/1, v/v) at 40 °C, respectively. The results are summarized in Table 1. The SEC RI traces of PIB(AllylCl)$_1$, intermediate *ω*-functional PIB with two *tert*-butyldimethylsilyloxymethylphenyl (SMP) groups (PIB(SMP)$_2$), and with two benzyl bromide (BnBr) moieties (PIB(BnBr)$_2$) show sharp monomodal distributions (see Figure 1). They are almost identical in shape and distribution. In the ^{1}H NMR spectrum of PIB(SMP)$_2$, there is no signal at 3.98 ppm corresponding to two methylene protons of the allyl chloride moiety and new signals at 0.05 and 4.59 ppm corresponding to SiCH$_3$ and ArC*H*$_2$OSi protons of the SMP

Scheme 1. Synthesis of ω-Functional PIBs with Benzyl Bromide Moieties (PIB(BnBr)$_n$) (Series 1)

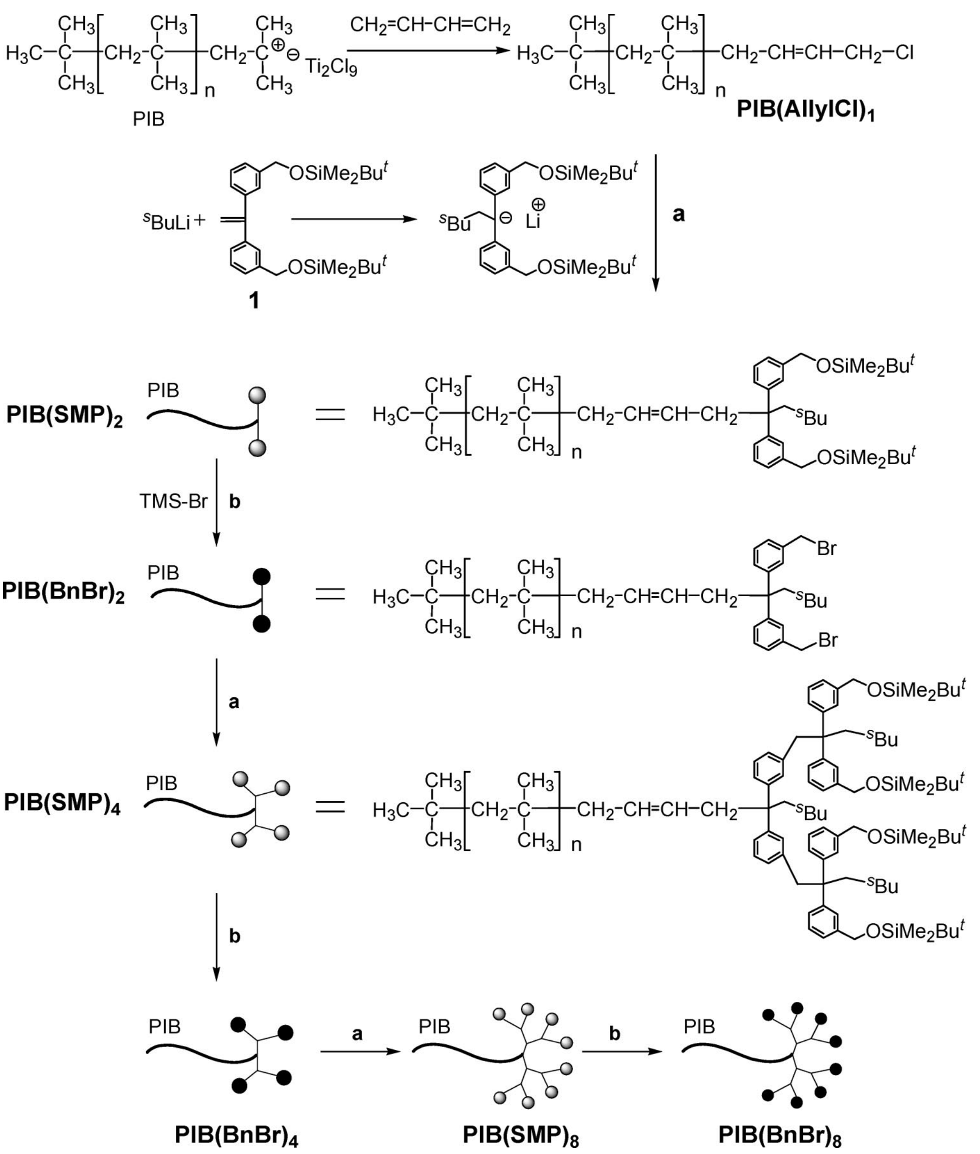


Table 1. Synthesis of ω-Functional PIBs with *tert*-Butyldimethylsilyloxymethylphenyl Groups (PIB(SMP)$_n$) and with Benzyl Bromide Moieties (PIB(BnBr)$_n$)

	M_n (kg/mol)			M_w/M_n	functionality	
type	theor	SEC	^{1}H NMR	SEC	theor	^{1}H NMR
PIB(SMP)$_2$	6.24	5.43	6.40	1.06	2	1.9_6
PIB(BnBr)$_2$	6.14	5.70	6.38	1.06	2	2.0_0
PIB(SMP)$_4$	7.05	5.81	7.01	1.06	4	4.0_0
PIB(BnBr)$_4$	6.85	5.90	7.03	1.07	4	3.9_0
PIB(SMP)$_8$	8.67	7.38	8.20	1.06	8	7.8_9
PIB(BnBr)$_8$	8.26	7.97	8.01	1.06	8	7.9_3

groups are clearly observed as shown in Figure 2. The ^{1}H NMR spectrum of PIB(BnBr)$_2$ shows the complete absence of the signals for SMP groups and the presence of a new signal at 4.35 ppm assigned to two methylene protons of the benzyl bromide moiety. The degrees of chain-end functionalization are virtually quantitative (f = 1.96 (SMP), 2.00 (BnBr)). All the results indicate the successful synthesis of well-defined PIB(BnBr)$_2$.

The same reaction sequences were repeated two more times to afford PIB(BnBr)$_4$ and PIB(BnBr)$_8$. These polymers exhibit sharp monomodal SEC distributions. The M_n values of the polymers determined by SEC-RALLS agreed well with the calculated ones (see Table 1). As can be seen in Figure 3, the expanded ^{1}H NMR spectra between 4.0 and 5.0 ppm show complete shift of the resonances for SMP and BnBr groups alternatively. The degrees of chain-end functionalization determined by ^{1}H NMR spectra are nearly quantitative in both cases (f = 3.90 (PIB(BnBr)$_4$), 7.93 (PIB(BnBr)$_8$)). The structure of

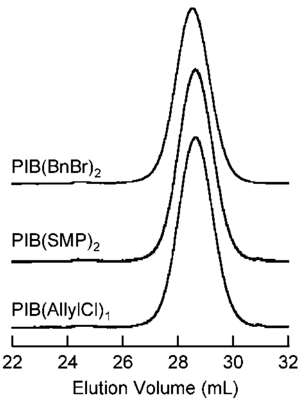


Figure 1. SEC RI traces of ω-functional PIBs with an allyl chloride moiety (PIB(AllylCl)$_1$), with two *tert*-butyldimethylsilyloxymethylphenyl groups (PIB(SMP)$_2$), and with two benzyl bromide moieties (PIB(BnBr)$_2$).

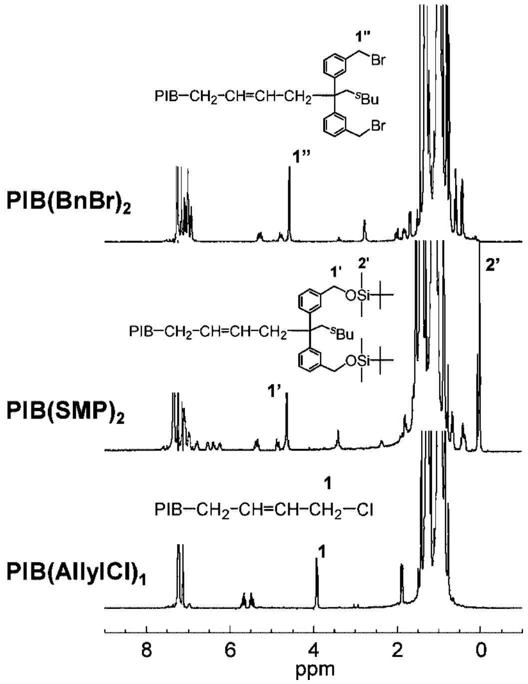


Figure 2. ^{1}H NMR spectra of ω-functional PIBs with an allyl chloride moiety (PIB(AllylCl)$_1$), with two *tert*-butyldimethylsilyloxymethylphenyl groups (PIB(SMP)$_2$), and with two benzyl bromide moieties (PIB(BnBr)$_2$).

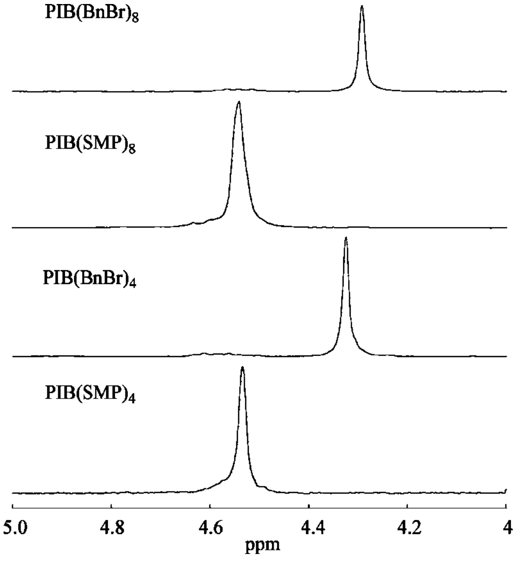


Figure 3. ^{1}H NMR spectra of ω-functional PIBs with *tert*-butyldimethylsilyloxymethylphenyl groups (PIB(SMP)$_n$) and with benzyl bromide moieties (PIB(BnBr)$_n$) (n = 4 and 8).

the functional polymers was corroborated by MALDI-TOF mass spectroscopy. Figure 4 shows the MALDI-TOF mass spectrum of PIB(SMP)$_8$, exhibiting a uniform series of peaks and the expected mass difference (56.1) corresponding to isobutylene unit. For instance, the peak at m/z 6226.8 corresponds to the Na$^+$ adduct of 57 mer for PIB(SMP)$_8$, whereas the calculated mass = 6227.3 Da (57.11 (C_4H_9) + 56.108 (IB) × 57 (units) + 54.09 ($-CH_2CH{=}CH-CH_2-$) + 2894.93 (dendritic part, $C_{188}H_{281}O_8Si_8$) + 22.99 (Na$^+$)). Unfortunately, the measurements of PIB(BnBr)$_n$ were not successful probably due to the partial decomposition of benzyl bromide moieties. In summary, all analytical results clearly indicate that the iterative reactions proceeded satisfactorily to afford a series of the expected ω-functional PIBs with a definite number (2, 4, and 8) of benzyl bromide moieties (series 1).

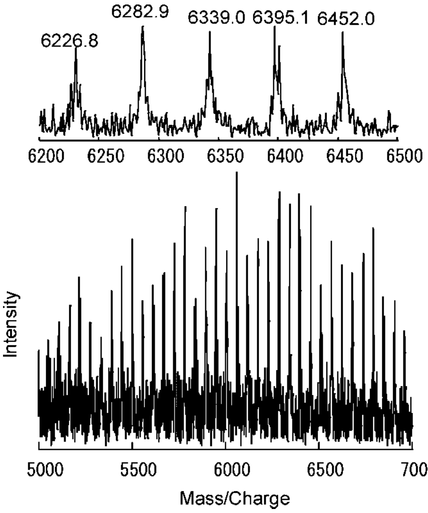


Figure 4. MALDI-TOF MASS spectra of ω-functional PIBs with eight *tert*-butyldimethylsilyloxymethylphenyl groups (PIB(SMP)$_8$).

Synthesis of α,ω-Functional Polyisobutylenes with 2, 4, and 8 Benzyl Bromide Moieties (Series 2). The synthesis of α,ω-functional PIBs with 2, 4, and 8 BnBr moieties ((BnBr)$_n$-PIB(BnBr)$_n$; n = 2, 4, and 8, series 2) was illustrated in Scheme 2. The method is the same as PIB(BnBr)$_n$ (series 1) except for employing α,ω-functional PIBs with allyl chloride moieties ((AllylCl)$_1$PIB(AllylCl)$_1$, M_n = 35 200, PDI = 1.04) as a starting material. The coupling reaction of (AllylCl)$_1$PIB(AllylCl)$_1$ with the functional 1,1-diphenylalkyl anion from **1** and ^{s}BuLi was carried out in THF at −78 °C. The subsequent transformation reaction with TMS-Br in chloroform/acetonitrile (4/1, v/v) at 40 °C was then performed. This iterative reaction sequence was repeated two more times. The results are summarized in Table 2. The SEC RI traces of the series 2 show sharp and symmetrical distributions (see Figure 5). The M_n values determined by SEC-RALLS agree fairly well with those calculated. The degrees of chain-end functionalization are practically quantitative (f = 3.99 ((BnBr)$_2$PIB(BnBr)$_2$), 7.90 ((BnBr)$_4$PIB(BnBr)$_4$), and 16.0 ((BnBr)$_8$PIB(BnBr)$_8$)). All analytical data of the resulting polymers indicate that the expected (BnBr)$_2$PIB(BnBr)$_2$, (BnBr)$_4$PIB(BnBr)$_4$, and (BnBr)$_8$PIB(BnBr)$_8$ could be successively synthesized (series 2). Thus, the iterative methodology could also be applied to the synthesis of α,ω-functional PIBs with multiple benzyl bromide moieties. It is noteworthy that novel chain end(s) multifunctional PIBs with a wide variety of functional groups can possibly be synthesized via highly reactive BnBr moieties.

Synthesis of A$_2$B, A$_4$B, and A$_8$B Type Asymmetric Star Polymers (A = Poly(methyl methacrylate) and B = Polyisobutylene, Series 3). As reported previously,[14] the benzyl moieties of chain-end functional polymers cleanly and quantitatively coupled with living poly(methyl methacrylate) (PMMA) in THF at −40 °C to afford a variety of star-branched polymers. Therefore, A$_2$B, A$_4$B, and A$_8$B asymmetric star polymers (series 3) could be synthesized by the coupling reaction of living PMMA with either of PIB(BnBr)$_n$; n = 2, 4, and 8, series 1. The synthetic routes are shown in Scheme 3. The coupling reactions were carried out in THF at −40 °C. A 2.5-fold excess of living PMMA to benzyl bromide moiety was always used to force the reaction to completion. The M_n values of living PMMA were designed to be around 10 000. The reaction proceeded efficiently within 24 h in all cases. The SEC RI profile of each reaction mixture shows only two sharp peaks corresponding to

Scheme 2. Synthesis of α,*ω*-Functional PIB with Benzyl Bromide Moieties ((BnBr)$_n$PIB(BnBr)$_n$) (Series 2)

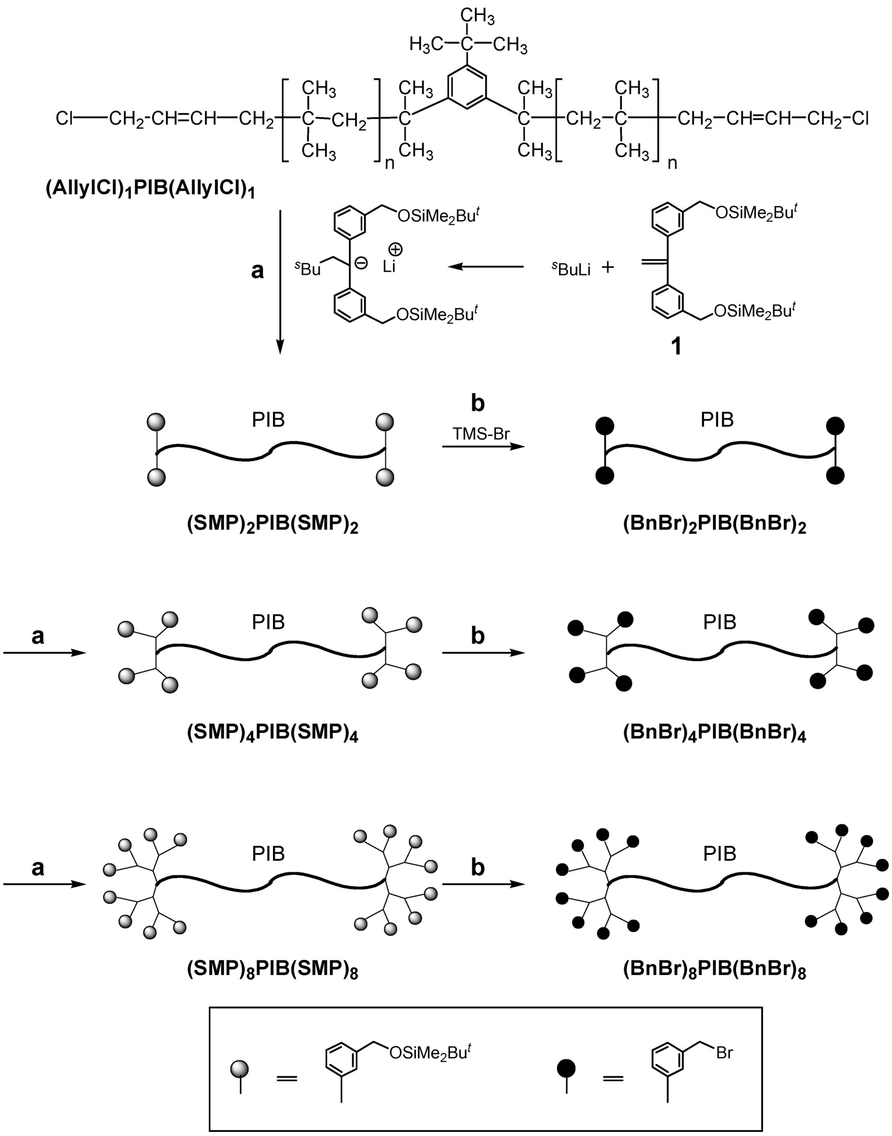


Table 2. Synthesis of α,*ω*-Functional PIB with *tert*-Butyldimethylsilyloxymethylphenyl Groups ((SMP)$_n$PIB(SMP)$_n$) and with Benzyl Bromide Moieties ((BnBr)$_n$PIB(BnBr)$_n$)

	M_n (kg/mol)			M_w/M_n	functionality	
type	theor	SEC	^{1}H NMR	SEC	theor	^{1}H NMR
(SMP)$_2$PIB(SMP)$_2$	36.1	30.0	34.3	1.04	4	3.9_7
(BnBr)$_2$PIB(BnBr)$_2$	35.9	31.5	35.3	1.04	4	3.9_9
(SMP)$_4$PIB(SMP)$_4$	37.7	33.1	36.9	1.04	8	8.0_0
(BnBr)$_4$PIB(BnBr)$_4$	37.3	38.1	36.8	1.05	8	7.9_0
(SMP)$_8$PIB(SMP)$_8$	40.9	39.8	40.1	1.04	16	$15._8$
(BnBr)$_8$PIB(BnBr)$_8$	40.1	40.6	39.8	1.04	16	$16._0$

the coupled product and the deactivated PMMA used in excess in the reaction (see Figure 6D–F). Neither intermediate polymer nor higher molecular weight shoulder was observed, indicating effective coupling reaction. The coupled polymers eluted at a higher molecular weight region were isolated in more than 85% yield by fractional precipitation using THF/methanol (1/10) as a solvent/nonsolvent system. Each isolated polymer exhibits a sharp monomodal SEC curve, as shown in Figure 6G–I. ^{1}H NMR spectra of the polymers show the absence of the signal at 4.35 ppm assigned to the methylene protons of BnBr moieties after coupling reactions, which means that all of BnBr moieties reacted completely.

The absolute M_n values of star polymers determined by SEC-RALLS agreed quite well with those calculated. The expected composition of PIB/PMMA could be confirmed by ^{1}H NMR. These results are summarized in Table 3. A novel series of A$_2$B, A$_4$B, and A$_8$B type asymmetric star polymers where A and B

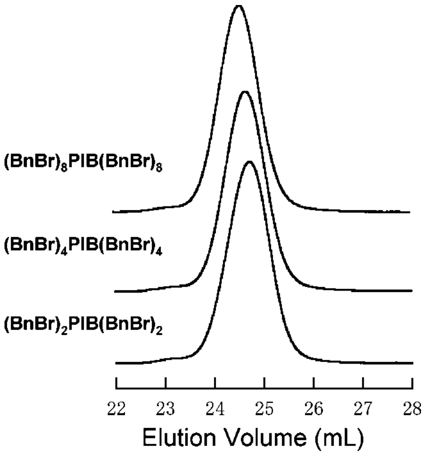
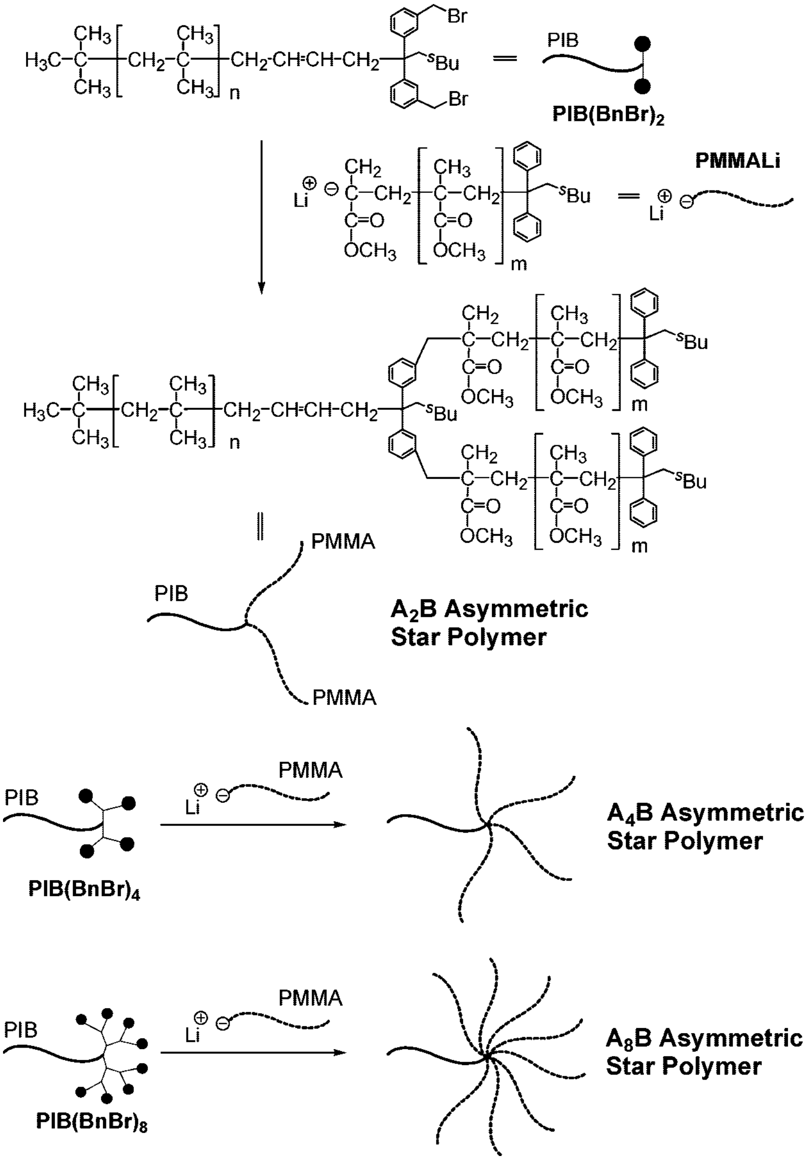


Figure 5. SEC RI traces of α,*ω*-functional PIBs with benzyl bromide moieties ((BnBr)$_n$PIB(BnBr)$_n$) (series 2).

Scheme 3. Synthesis of A_nB Type Asymmetric Star Polymers (Series 3)



were PMMA and PIB segments, respectively, was thus successfully synthesized. It should be mentioned that no steric limitation is encountered in the coupling reaction of living PMMA with each of $PIB(BnBr)_n$, series 1.

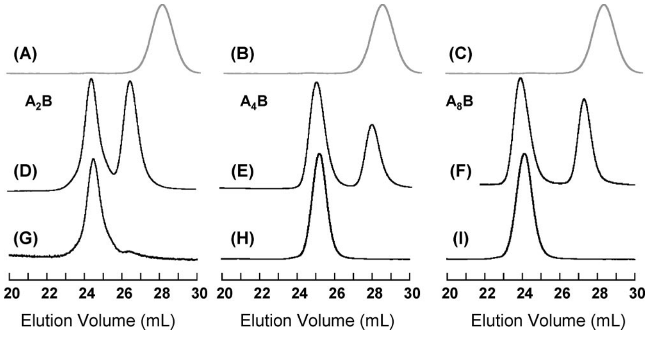


Figure 6. SEC RI traces of original ω-functional PIBs with two benzyl bromide moieties ($PIB(BnBr)_2$, (A−C)), crude polymers obtained by reactions of living PMMA with $PIB(BnBr)_n$ (series 1); (D) $n = 2$, (E) $n = 4$, and (F) $n = 8$, and the corresponding isolated A_nB type asymmetric star polymers; (G) $n = 2$, (H) $n = 4$, and (I) $n = 8$.

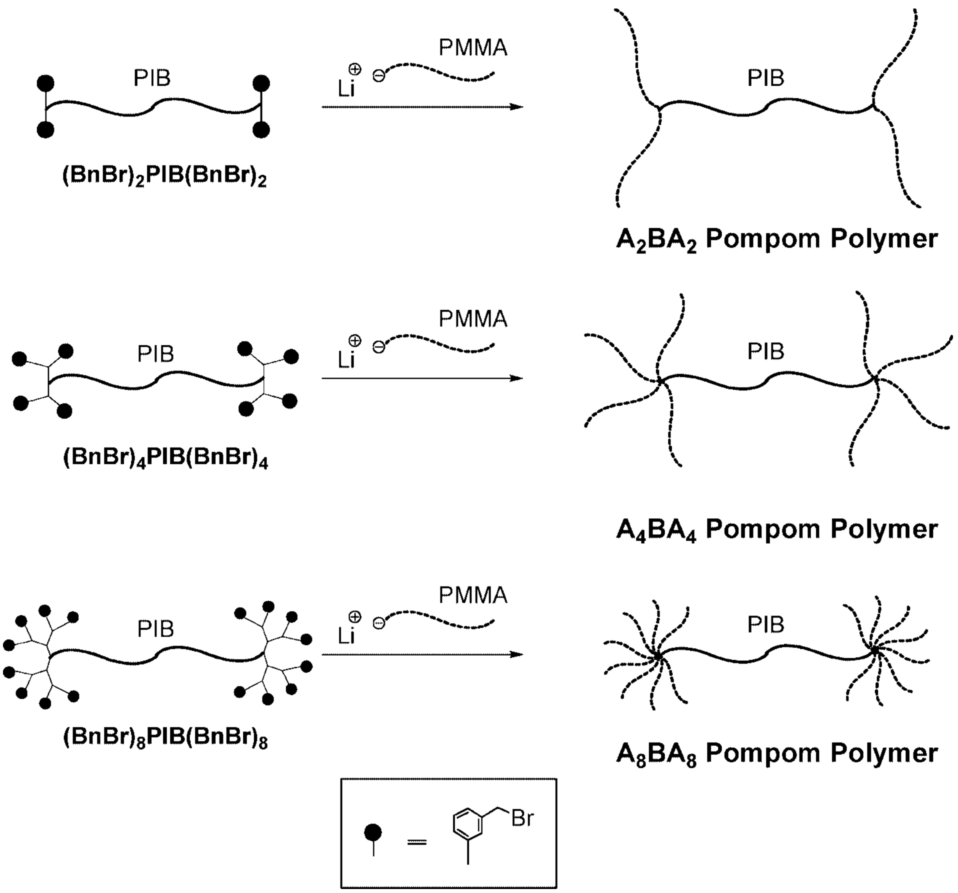
Synthesis of A_2BA_2, A_4BA_4, and A_8BA_8 Type Pompom Polymers (A = Poly(methyl methacrylate) and B = Polyisobutylene, Series 4). Pompom polymers are one of the interesting architectural block copolymers from not only a synthetic viewpoint but also specific viscoelastic properties and morphologies. Hadjichristidis and co-workers reported the synthesis of well-defined A_nBA_n type pompom polymers where A and B were polybutadiene (or polyisoprene) and polystyrene, respectively, based on living anionic polymerization utilizing silyl chloride linking reactions and investigated their viscoelastic properties.[15] Knauss and co-workers have developed a new synthetic method of pompom polymers by convergent living anionic polymerization using 4-(chlorodimethylsilyl)styrene as a dual monomer/coupling agent.[16] In this methodology, the arm number in pompom polymers is narrowly distributed but not exact. In this section, an array of A_2BA_2, A_4BA_4, and A_8BA_8 type pompom polymers where A and B are PMMA and PIB segments, respectively, has been synthesized by an alternative approach which includes the coupling reactions of $(BnBr)_n$-$PIB(BnBr)_n$ with living PMMA (see Scheme 4). Topological structures of A_nBA_n type pompom polymers can be categorized in a family of ABA triblock copolymers and of great interest

Table 3. Synthesis of A_nB Type Asymmetric Star Polymers (Series 3)

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (A/B wt %)	
type[a]	theor	RALLS	SEC	theor	RALLS	SEC	theor	^{1}H NMR
A_2B	25.1	25.7	26.2	26.6	27.2	1.06	62/38	63/37
A_4B	46.2	45.4	36.1	47.6	45.8	1.03	87/13	86/14
A_8B	117	123	59.7	119	124	1.02	95/5	94/6

[a] A and B are PMMA and PIB, respectively.

Scheme 4. Synthesis of A_nBA_n Type Pompom Polymers (Series 4)



due to possible behaviors as thermoplastic elastomers (TPEs) in which hard PMMA (A) domains act as a physical cross-linker in a soft PIB (B) matrix. This hard/soft combination should be very important, especially for biomedical applications taking the biocompatibility of both segments into consideration.

The coupling reactions between $(BnBr)_nPIB(BnBr)_n$ ($n = 2$, 4, and 8, series 2) and excess living PMMA were carried out in THF at −40 °C for 24 h to synthesize the desired pompom polymers. A 2-fold excess of living PMMA to BnBr moieties was always used. The M_n values of living PMMA were designed so that the weight composition, PIB/PMMA, is between 63/37 and 75/25, which normally provides good mechanical properties for a linear PMMA-*b*-PIB-*b*-PMMA triblock copolymer as TPE. There are only the expected two peaks corresponding to the coupled product and the deactivated PMMA used in excess in the SEC RI trace of each reaction mixture (see Figure 7A−C).

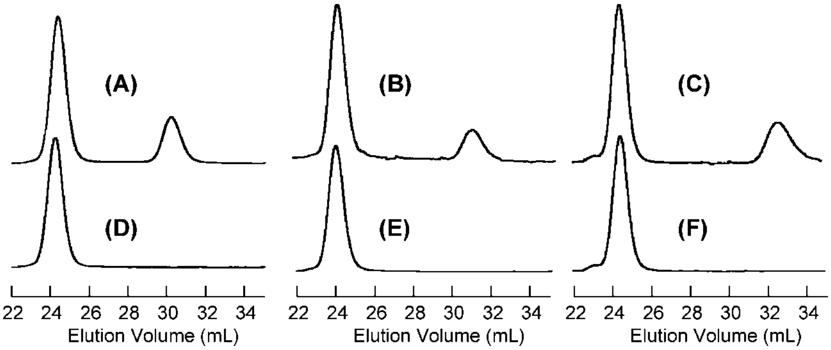


Figure 7. SEC RI traces of crude polymers obtained by reactions of living PMMA with α,ω-functional PIBs with benzyl bromide moieties ($(BnBr)_nPIB(BnBr)_n$, series 2); (A) $n = 2$, (B) $n = 4$, and (C) $n = 8$, and the corresponding isolated A_nBA_n type pompom polymers; (D) $n = 2$, (E) $n = 4$, and (F) $n = 8$.

Table 4. Synthesis of A_nBA_n Type Pompom Polymers (Series 4)

	M_n (kg/mol)			M_w (kg/mol)		M_w/M_n	composition (A/B wt %)	
type[a]	theor	RALLS	SEC	theor	RALLS	SEC	theor	^{1}H NMR
A_2BA_2	49.1	50.2	51.1	50.1	51.0	1.02	28/72	28/72
A_4BA_4	55.5	55.0	51.8	56.6	55.6	1.02	37/63	37/63
A_8BA_8	50.7	53.1	49.8	52.2	54.5	1.03	25/75	24/76

[a] A and B are PMMA and PIB, respectively.

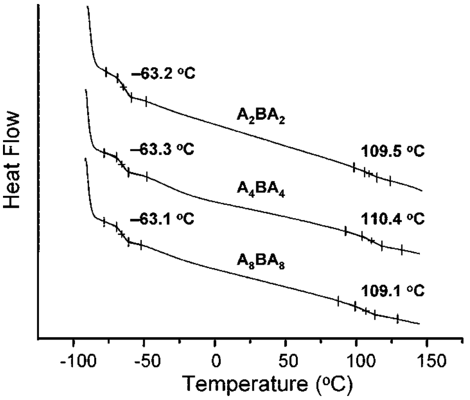


Figure 8. DSC thermograms of A_nBA_n type pompom polymers (series 4).

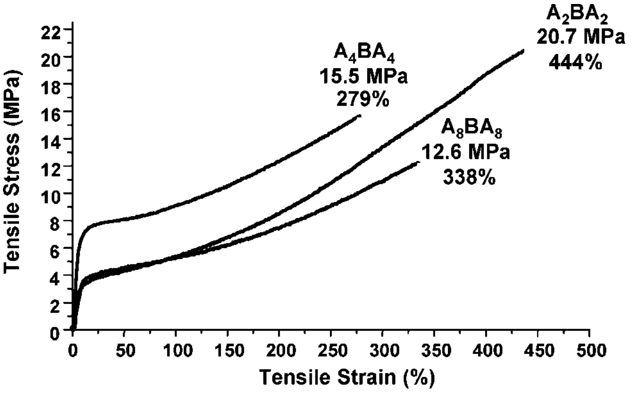


Figure 9. Stress−strain plots for the films of A_nBA_n type pompom polymers (series 4).

The coupled polymers were isolated in more than 90% yield by fractional precipitation using THF/methanol (1/10) as a solvent/nonsolvent system. A sharp monomodal curve for each isolated polymer was confirmed by SEC, as shown in Figure 7D−F. ^{1}H NMR spectra of the polymers showed the absence of the unreacted BnBr moieties and the reasonable intensity ratio for PIB and PMMA main chains. The results are summarized in Table 4. The absolute M_n values of coupled polymers determined by SEC-RALLS are in good agreement with those calculated. All of the results reveal the successful synthesis of novel A_2BA_2, A_4BA_4, and A_8BA_8 type pompom polymers with PMMA and PIB segments.

DSC thermograms of series 4 are shown in Figure 8. For all samples, there are two glass transition temperatures, one at −63 °C corresponding to PIB domains and the other at 109−110 °C corresponding to PMMA domains, suggesting microphase-separated morphologies. Stress−strain plots of cast films of the samples were obtained by dynamic-mechanical measurements (see Figure 9). All A_nBA_n type pompom polymers show good elastomeric properties (279−444% ultimate elongations and 12.6−20.7 MPa tensile strengths) comparable to typical ABA type PIB-based TPEs.[17]

Conclusions

A novel series of multifunctional PIBs with 2, 4, and 8 benzyl bromide moieties at ω-chain end or α,ω-chain ends has been successfully synthesized by the iterative divergent methodology previously developed for the synthesis of chain-end functional polystyrenes with benzyl bromide moieties. PIBs with ω- and α,ω-allyl halide moiety (moieties) were effective starting materials. By using multifunctional PIBs with BnBr moieties in coupling reactions of living PMMA, a new series of A_2B, A_4B, and A_8B type asymmetric star polymers as well as A_2BA_2, A_4BA_4, and A_8BA_8 type pompom polymers where A and B are PMMA and PIB segments, respectively, have been synthesized successfully. SEC-RALLS and ^{1}H NMR analyses of the resulting branched polymers confirmed their well-defined structures and low degrees of compositional heterogeneity. DSC measurements and the mechanical testing of A_nBA_n type pompom polymers confirmed their phase-segregated structure and elastomeric properties. In the iterative divergent methodology, further repeating the iterative reaction sequence can increase the number of benzyl bromide moieties, and thereby star and pompom polymers with more arms may possibly be synthesized.

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