Synthesis of Asymmetric Star-Branched Polymers Having Two Polyacetylene Arms by Means of Living Anionic Polymerization Using 1,1-Diphenylethylene Derivatives

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ABSTRACT: Two series of new 3-arm AE_2, 4-arm ABE_2, 5-arm $ABCE_2$, and 5-arm AD_2E_2, 6-arm ABD_2E_2, 7-arm $ABCD_2E_2$ asymmetric star-branched polymers have been synthesized using living anionic polymers and 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide. The A, B, C, D, and E arms were polystyrene (A), poly(α-methylstyrene) (B), poly(4-methoxystyrene) (C), poly(4-trimethylsilylstyrene) (D), and poly(4-methylphenylvinyl sulfoxide) (E) segments. The methodology involves an addition reaction of either *sec*-BuLi or poly(4-trimethylsilylstyryl)lithium with two 1,1-diphenylethylene (DPE)-chain-functionalized polymers and a subsequent living anionic polymerization of 4-methylphenylvinyl sulfoxide in situ initiated with the two 1,1-diphenylalkyl anions generated by the addition reaction. Three DPE-functionalized polymers herein used were chain-end-functionalized polystyrene, in-chain-functionalized AB diblock copolymer, and core-functionalized 3-arm ABC star-branched polymer with two DPE moieties at chain end, junction between blocks, and core position, respectively. The molecular characterization results revealed a high degree of structural and compositional homogeneity in each of all the resulting asymmetric star-branched polymers. By thermal treatment of these stars at 150 °C, the two poly(4-methylphenylvinyl sulfoxide) arms introduced into each star were completely converted to polyacetylene segments as confirmed by FT-IR, elemental analysis, and TGA measurements. Thus, novel six asymmetric star-branched polymers having two polyacetylene arms could be successfully synthesized.

Introduction

Block copolymers possessing conductive π-conjugated polymer segments have attracted much attention because of their unique physical and mechanical properties in bulk and solution originating from rigid-rod-like structures of the π-conjugated polymer segments.[1−7] Furthermore, each block segment tends to phase-separate at molecular level, followed by self-organizing to form nanoscopic periodic specially shaped domains and supramolecular assemblies which have many potential applications in the area of molecular electronic and optical devices.[8,9] Among such conductive π-conjugated polymers, polyacetylene (PA) is one of the most well-known polymers exhibiting high conductivity and large third-order nonlinear optical activity. However, the direct synthesis of well-defined block copolymers with PA segments is problematic because of the ill-controlled polymerization of acetylene and intact ability and insolubility of the PA chains. In order to overcome these problems, a soluble precursor route was developed by means of ring-opening metathesis polymerization of specially designed monomers such as 7,8-bis(trifluoromethyl)tricycle[4.2.2.0^{2,5}]deca-3,7,9-triene and benzvalene.[10−14] The resulting polymers with controlled chain structures could be completely converted to PA segments under appropriate conditions. Unfortunately, such monomers are not stable and difficult to handle in operation.[10,12] Another attractive route is the living anionic sequential block copolymerization using phenylvinyl sulfoxide (PVSO) which has been developed by Hogen-Esch and co-workers.[15,16] The poly(phenylvinyl sulfoxide) (PPVSO) segment obtained by the anionic polymerization has several advantages like it is relatively stable, soluble in a variety of solvents, controllable in molecular weight, and readily convertible to PA simply by thermal treatment. A series of the block copolymers with PPVSO segments were prepared by several research groups and converted to the corresponding block copolymers with PA segments by the thermal treatment.[15−21] Conductive supramolecular assemblies derived from such block copolymers have also been reported.[22]

Compared to block copolymers, more structural variation is possible in asymmetric star-branched polymers whose arms differ in chemical structure due to their branched architectures in addition to heterophase structures.[23−30] Furthermore, novel and complex morphologies have been recently observed in the asymmetric star-branched polymers.[29,31−42] It is therefore expected that if PPVSO segment(s) can be introduced into an asymmetric star-branched polymer, the resulting asymmetric star-branched polymer may become a more attractive conductive material. For this reason, we planned the synthesis of asymmetric star-branched polymers having PA arm by using the recently developed iterative methodology[43−49] in conjunction with the living anionic polymerization of PVSO. In practice, such asymmetric stars have been synthesized by developing the iterative methodology which involves a linking reaction of living anionic polymers with 1,1-diphenylethylene (DPE)-chain-functionalized polymers and a subsequent living anionic polymerization of 4-methylphenylvinyl sulfoxide (MPVSO)[50] with the generated anion after the linking reaction, followed by thermal treatment of the resulting asymmetric stars. Thus, a series of novel well-defined 3-arm ABC, 4-arm ABCD, and even 5-arm ABCDE asymmetric star-branched polymers having PA arm have been successfully obtained.[47]

As a succeeding study, we report herein on the synthesis of two series of novel 3-arm AE_2, 4-arm ABE_2, and 5-arm $ABCE_2$ as well as 5-arm AD_2E_2, 6-arm ABD_2E_2, and 7-arm $ABCD_2E_2$ asymmetric stars having two PA arms by the similar methodol-

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ogy using chain-functionalized polymers with two DPE moieties. The A, B, C, D, and E arms were polystyrene (A), poly(α-methylstyrene) (B), poly(4-methoxystyrene) (C), poly(4-trimethylsilylstyrene) (D), and poly(4-methylphenylvinyl sulfoxide) (E) segments, respectively.

Experimental Section

Materials. All the reagents (>98% purities) were purchased from Tokyo Kasei Kogyo Co. Ltd. or Aldrich, Japan, and used as received unless otherwise stated. Tetrahydrofuran (THF) was refluxed over sodium wire, distilled over $LiAlH_4$ under nitrogen, and then distilled from its sodium naphthalenide solution in vacuo (10^{-6} Torr). 1,1-Diphenylethylene (DPE) was distilled over CaH_2 under reduce pressure and then distilled from its *n*-butyllithium solution in vacuo (10^{-6} Torr). Styrene (S), α-methylstyrene (αMS), 4-methoxystyrene (MOS), and 4-trimethylsilylstyrene (TMSS) were washed with 10% NaOH aqueous solution, dried over $MgSO_4$, and distilled over CaH_2 under reduced pressures. The monomers were finally distilled over dibutylmagnesium (Bu_2Mg) (3−5 mol %) on the vacuum line into ampules equipped with break-seals that were prewashed with potassium naphthalenide in THF. *N,N*-Dimethylformamide (DMF) was distilled over CaH_2 under reduced pressure. Lithium bromide (LiBr) was dried at 110 °C overnight in vacuo (10^{-6} Torr). 4-(3-Bromopropyl)benzophenone and 4-methylphenylvinyl sulfoxide (MPVSO) were synthesized and purified as previously reported. Both DPE-chain-end-functionalized polystyrene (PS-D) and DPE-in-chain-functionalized polystyrene-*block*-poly(α-methylstyrene) (PS-D-PαMS) were synthesized according to the procedure reported previously.[47,51]

Measurements. All ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in $CDCl_3$ on a Bruker DPX 300 spectrometer. Size exclusion chromatography (SEC) was performed on a Tosoh HLC 8020 instrument equipped with UV (254 nm) and refractive index (RI) detectors. THF was used as an eluent with a flowing rate of 1.0 mL/min at 40 °C. Three polystyrene columns (TSK_{gel} G4000H_{XL}, TSK_{gel} G3000H_{XL}, TSK_{gel} G2000H_{XL} or TSK_{gel} G5000H_{XL}, TSK_{gel} G4000H_{XL}, TSK_{gel} G3000H_{XL}) were used. Measurable molecular weight ranges are $10^3-4 \times 10^4$ and $5 \times 10^3-4 \times 10^5$ g/mol, respectively. Polystyrene standards were used for calibration of the SEC instrument. Static light scattering (SLS) measurements were performed on an Otsuka Electronics DLS-7000 instrument equipped with a He−Ne laser (633 nm) in THF at 25 °C. The refractive index increment (d*n*/d*c*) in THF at 25 °C was determined with an Otsuka Electronics DRM-1020 refractometer operating at 633 nm. FT-IR analyses were performed on a Jasco FT/IR-460 spectrometer. Thermogravimetric analysis (TGA) was conducted on a Seiko EXSTAR 6000-TG/DTA 6300 thermogravimetric analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere.

Synthesis of 1-(4-(3-Bromopropyl)phenyl)-1-phenylethylene (DBr). To a solution of methyltriphenylphosphonium bromide (13.6 g, 38.0 mmol) and potassium *tert*-butoxide (4.26 g, 38.0 mmol) in THF (50 mL), a portion of 4-(3-bromopropyl)benzophenone (9.20 g, 30.4 mmol) in THF (20 mL) was added dropwise at 0 °C under a nitrogen atmosphere. The reaction mixture heated to room temperature and kept under stirring for 6 h, poured into water, and extracted with ether thrice. The ethereal layer was washed with aqueous $NaHCO_3$ and brine and then dried over $MgSO_4$. After filtration, the ethereal layer was poured into hexane to remove triphenylphosphine oxide. Flash column chromatography (hexane/ethyl acetate = 50:1−10:1, v/v) gave DBr in 70% yield (6.40 g, 21.2 mmol). ^1H NMR ($CDCl_3$): δ 7.14−7.33 (m, 9H, ArH), 5.42 (d, J 7, 2H, CH_2=), 3.41 (t, J 7, 2H, CH_2Br), 2.79 (t, J 8, 2H, $CH_2CH_2CH_2Br$), 2.18 (m, 2H, CH_2CH_2Br). ^{13}C NMR ($CDCl_3$): δ 149.8, 141.6, 140,2, 139.4, 128.4, 128.3, 128.2, 127.7, 114.0, 34.1, 33.7, 33.1. Elemental analysis: Calcd for $C_{17}H_{17}Br$: C, 67.78; H, 5.69; Br, 26.53. Found: C, 67.92; H, 5.70; Br, 26.50.

Synthesis of 3,5-Bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl Bromide (D_2Br). A mixture of DBr (5.00 g, 16.6 mmol), 3,5-dihydroxybenzyl alcohol (0.950 g, 6.78 mmol), and potassium carbonate (3.00 g, 21.7 mmol) in 60 mL of dry DMF was stirred at 70 °C under nitrogen for 18 h. The mixture was cooled down to room temperature, poured into water, and then extracted with ether thrice. The combined extracts were washed with water, 5% $NaHCO_3$, and brine and dried over $MgSO_4$ overnight. The crude product was purified by flash column chromatography (hexane/ethyl acetate = 5:1−2:1, v/v), and 3.00 g (5.16 mmol, 76%) of 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl alcohol (D_2-OH) was obtained.

D_2OH: ^1H NMR ($CDCl_3$): 7.15−7.33 (m, 18H, ArH), 6.51 (s, 2H, ArH), 6.39 (s, 1H, ArH), 5.44 (d, J 10, 4H, CH_2=), 4.61 (s, 2H, CH_2OH), 3.96 (t, J 6, 4H, CH_2O), 2.81 (t, J 8, 4H, $CH_2CH_2CH_2O$), 2.10 (m, 4H, CH_2CH_2O). ^{13}C NMR ($CDCl_3$): 160.4, 149.8, 143.3, 141.6, 141.2, 139.2, 128.4, 128.2, 127.7, 113.9, 105.2, 100.6, 67.0, 65.4, 31.9, 30.8. Elemental analysis: Calcd for $C_{41}H_{40}O_3$: C, 84.79; H, 6.94. Found: C, 84.82; H, 6.95.

The resulting D_2OH (2.90 g, 5.00 mmol) was added to a THF (30 mL) solution containing PPh_3 (2.62 g, 10.0 mmol) and CBr_4 (3.32 g, 10.0 mmol) under nitrogen. The reaction mixture was stirred for 30 min at room temperature, concentrated, and extracted with ether thrice, and the combined organic phases were dried over $MgSO_4$. Flash column chromatography (hexane/ethyl acetate = 80:1−50:1, v/v) gave D_2Br in 63% yield (2.04 g, 3.17 mmol).

D_2Br: ^1H NMR ($CDCl_3$): 7.16−7.33 (m, 18H, ArH), 6.52 (s, 2H, ArH), 6.39 (s, 1H, ArH), 5.44 (d, J 10, 4H, CH_2=), 4.40 (s, 2H, CH_2Br), 3.96 (t, J 6, 4H, CH_2O), 2.81 (t, J 8, 4H, $CH_2CH_2CH_2O$), 2.10 (m, 4H, CH_2CH_2O). ^{13}C NMR ($CDCl_3$): 160.3, 149.9, 141.7, 141.1, 139.7, 139.2, 128.4, 128.2, 127.7, 113.9, 107.6, 101.6, 67.1, 33.8, 31.9, 30.7. Elemental analysis: Calcd for $C_{41}H_{39}BrO_2$: C, 76.51; H, 6.11; Br, 12.41. Found: C, 76.60; H, 6.15; Br, 12.40.

Synthesis of Chain-Functionalized Polymers with Two DPE Moieties. (1) Chain-End-Functionalized Polystyrene with Two DPE Moieties (PS-D_2). Under high-vacuum conditions, to a THF (22.4 mL) solution of polystyryllithium (PSLi) (2.18 g, 0.208 mmol, $\bar{M}_n$(SEC) = 10 500 g/mol), a THF (5.40 mL) solution of DPE (0.320 mmol) was added at −78 °C and allowed to react for 1 h. To the reaction mixture was then added a THF solution (6.00 mL) of D_2-Br (0.306 mmol) which was prepurified by adding Bu_2Mg (0.102 mmol) for 1 h at room temperature. After 15 min, the resultant polymer was poured into a large amount of methanol. The polymer was precipitated from THF into methanol thrice and freeze-dried from its dry benzene solution for 36 h. Chain-end-functionalized polystyrene with two DPE moieties (PS-D_2) was thus obtained: 2.24 g, yield 96%, $\bar{M}_n$(SEC) = 11 200 g/mol, $\bar{M}_w/\bar{M}_n$ = 1.02, DPE functionality (*F*) = 2.02. ^1H NMR ($CDCl_3$): δ 6.32−7.41 (broad, 370H, ArH), 5.46 (d, J 10, 2H, CH_2=), 1.05−2.35 (broad, 254H, CH_2 and CH), 0.59−0.81 (broad, 6H, $CH_3CH_2CH(CH_3)$).

(2) In-Chain-Functionalized Polystyrene-*block*-poly(α-methylstyrene) with Two DPE Moieties between Two Blocks (PS-D_2-PαMS). To a THF (23.0 mL) solution of poly(α-methylstyryl)lithium (PαMSLi) (2.08 g, 0.208 mmol, $\bar{M}_n$(SEC) = 10 000 g/mol) was added a THF solution (21.8 mL) of PS-D (1.78 g, 0.188 mmol) at −78 °C, and the reaction was conducted for 4 h. After adding a THF (4.72 mL) solution of DPE (0.260 mmol) and allowing the reaction mixture for 1 h at −78 °C, the resulting polymer anions were reacted with D_2Br (0.338 mmol) in THF (6.60 mL) prepurified by adding Bu_2Mg (0.118 mmol) for 1 h at room temperature. After 30 min, the resulting polymers were poured into a large amount of methanol. The linked polymer was isolated in 85% yield (3.18 g) by fractional precipitation using hexane and cyclohexane. After precipitating from THF into methanol thrice and freeze-drying with dry benzene for 36 h, polystyrene-*block*-poly(α-methylstyrene) functionalized with two DPE moieties between two blocks (PS-D_2-PαMS) was obtained: $\bar{M}_n$(SEC) = 20 400 g/mol, $\bar{M}_w/\bar{M}_n$ = 1.01, *F* = 2.00. ^1H NMR ($CDCl_3$): δ 6.31−7.42 (broad, 880H, ArH), 5.47 (d, J 10, 2H, CH_2=), 1.24−2.14 (broad, 535H, CH_2 and CH), 0.61−0.83 (broad, 12H, $CH_3CH_2CH(CH_3)$), 0.02−0.56 (broad, 254H, α-CH_3).

(3) Core-Functionalized 3-Arm ABC Star-Branched Polymer with Two DPE Moieties. To a THF (10.8 mL) solution of poly(4-methoxystyryl)lithium (PMOSLi) (1.47 g, 0.150 mmol, $\bar{M}_n$(SEC)

= 9800 g/mol), a THF solution (19.2 mL) of PS-D-PαMS (1.96 g, 0.0975 mmol) was added at −78 °C, and the reaction was conducted at −78 °C for 12 h. After adding a THF (2.40 mL) solution of DPE (0.250 mmol) and allowing to react for an additional 1 h, the resulting polymer anions were reacted with D_2Br (0.204 mmol) in THF (4.40 mL) prepurified by adding Bu_2Mg (0.102 mmol) for 1 h at room temperature. After 1 h, the resulting polymers were poured into a large amount of methanol. The objective star polymer was isolated in 87% yield (2.60 g) by fractional precipitation using toluene (200 mL) and methanol (90 mL). After precipitating from THF into methanol thrice and freeze-drying with dry benzene for 36 h, a 3-arm polystyrene−poly(α-methylstyrene)−poly(4-methoxystyrene) star-branched polymer core-functionalized with two DPE moieties (PS−PαMS−PMOS) was obtained: $\bar{M}_n$(^{1}H NMR) = 30 100 g/mol, $\bar{M}_w/\bar{M}_n$ = 1.01, F = 2.01. ^{1}H NMR ($CDCl_3$): δ 6.28−7.41 (broad, 1300H, ArH), 5.44 (d, J 10, 2H, CH_2=), 3.68−3.82 (broad, 216H, OCH_3), 1.05−2.39 (broad, 954H, CH_2 and CH), 0.61−0.81 (broad, 18H, C*H*$_3$CH$_2$CH(C*H*$_3$)), 0.00−0.54 (broad, 250H, α-CH_3).

Synthesis of 3-Arm AE$_2$, 4-Arm ABE$_2$, and 5-Arm ABCE$_2$ Asymmetric Stars Having Two PMPVSO Arms. (1) 3-Arm AE$_2$ Star-Branched Polymer. To a heptane (2.70 mL) solution of *sec*-butyllithium (*sec*-BuLi) (0.135 mmol), a THF (11.1 mL) solution of PS-D$_2$ (0.398 g, 0.0415 mmol) was added at −78 °C and allowed to react for 4 h. A THF (2.90 mL) solution of DPE (0.197 mmol) was introduced to the reaction systems at −78 °C for 1 h to cap the excess *sec*-BuLi, and then a THF (7.00 mL) solution of LiBr (2.10 mmol) was added to the mixture. After 30 min, MPVSO (1.59 g, 9.56 mmol) in THF (15.9 mL) was added to polymerize at −78 °C for 24 h. The reaction was quenched with degassed methanol and recovered by precipitation into a large amount of hexane. The polymer mixture was dissolved in 20 mL of THF and then poured into 300 mL of methanol. The 3-arm AE$_2$ star-branched polymer comprised of PS and two PMPVSO segments was totally precipitated, while the PMPVSO homopolymer remained in the solution. After freeze-drying with dry benzene, 3-arm AE$_2$ star-branched polymer was obtained in 98% yield (1.31 g). A homopolymer of MPVSO was recovered in more than 90% yield by evaporating the methanol solution, followed by precipitation in hexane. ^{1}H NMR ($CDCl_3$): δ 6.00−8.09 (broad, 1140H, ArH), 2.18−2.58 (broad, 435H, ArC*H*$_3$), 1.05−2.15 (broad, 730H, CH_2 and CH), 0.50−0.82 (broad, 18H, C*H*$_3$CH$_2$CH(C*H*$_3$)).

(2) 4-Arm ABE$_2$ Star-Branched Polymer. To a heptane (2.18 mL) solution of *sec*-BuLi (0.109 mmol), a THF (12.1 mL) solution of PS-D$_2$-PαMS (0.416 g, 0.0210 mmol) was added at −78 °C and allowed to react for 3 h. A THF (2.10 mL) solution of DPE (0.227 mmol) was introduced to the reaction system for 2 h at −78 °C, and a THF (6.20 mL) solution of LiBr (1.86 mmol) was then added. After 1 h, MPVSO (1.23 g, 7.38 mmol) in THF (12.3 mL) was added to polymerize at −78 °C for 24 h. By using the same procedure mentioned above, both ABE$_2$ star and PMPVSO were isolated in 99% (0.89 g) and 94% (0.71 g) yields, respectively. ^{1}H NMR ($CDCl_3$): δ 6.33−7.81 (broad, 1570H, ArH), 2.26−2.53 (broad, 410H, ArC*H*$_3$), 1.08−2.24 (broad, 807H, CH_2 and CH), 0.63−0.83 (broad, 24H, C*H*$_3$CH$_2$CH(C*H*$_3$)), 0.02−0.56 (broad, 255H, α-CH_3).

(3) 5-Arm ABCE$_2$ Star-Branched Polymer. To a heptane (2.56 mL) solution of *sec*-BuLi (0.128 mmol), a THF (13.2 mL) solution of core-functionalized PS−PαMS−PMOS star-branched polymer with two DPE moieties (0.843 g, 0.0280 mmol) was added at −78 °C and allowed to react for 4 h. A THF (3.40 mL) solution of DPE (0.367 mmol) was introduced to the reaction system at −78 °C for 2 h, and then a THF (7.17 mL) solution of LiBr (2.15 mmol) was added to the mixture. After 1 h, MPVSO (1.33 g, 8.00 mmol) in THF (13.3 mL) was added to polymerize at −78 °C for 24 h. By adopting the same process as above for the other stars, both ABCE$_2$ star and PMPVSO were isolated in 97% (1.39 g) and 98% (0.74 g) yields, respectively. ^{1}H NMR ($CDCl_3$): δ 6.20−7.80 (broad, 1940H, ArH), 3.62−3.86 (broad, 218H, OCH_3), 2.26−2.56 (broad, 380H, ArC*H*$_3$), 1.05−2.13 (broad, 1190H, CH_2 and CH), 0.58−0.80 (broad, 30H, C*H*$_3$CH$_2$CH(C*H*$_3$)), 0.00−0.53 (broad, 250H, α-CH_3).

Synthesis of 5-Arm AD$_2$E$_2$, 6-Arm ABD$_2$E$_2$, and 7-Arm ABCD$_2$E$_2$ Asymmetric Stars Having Two PMPVSO Arms. (1) Synthesis of 5-Arm AD$_2$E$_2$ Star-Branched Polymer. To a THF (8.75 mL) solution of poly(4-trimethylsilylstyryl)lithium (PTMSSLi) (1.39 g, $\bar{M}_n$(calcd) = 10 200 g/mol, $\bar{M}_n$(NMR) = 8570 g/mol, 0.162 mmol), a THF (14.1 mL) solution of PS-D$_2$ (0.504 g, 0.0526 mmol) was added at −78 °C and allowed to react for 20 h. A THF (3.01 mL) solution of DPE (0.204 mmol) was introduced to the reaction system at −78 °C for 2 h to end-cap the excess of PTMSSLi, and then a THF (6.53 mL) solution of LiBr (1.96 mmol) was added to the mixture. After 1 h, MPVSO (1.41 g, 8.52 mmol) in THF (14.1 mL) was added to polymerize at −78 °C for 24 h. The reaction was then quenched with degassed methanol, and the polymer mixture was precipitated by adding a large amount of hexane. To a solution of the polymer mixture dissolved in a small amount of THF, 150 mL of hexane was added, and then 200 mL of methanol was slowly added to the turbid solution. The objective 5-arm AD$_2$E$_2$ star-branched polymer comprised of PS, two PTMSS, and two PMPVSO arms was nearly completely precipitated, and the diblock copolymer, PTMSS-*block*-PMPVSO (PTMSS-*b*-PMPVSO), generated as a byproduct during the polymerization almost remained in the solution. The AD$_2$E$_2$ star-branched polymer was reprecipitated twice by the THF−methanol system and freeze-dried from its absolute benzene solution. The PTMSS-*b*-PMPVSO diblock copolymer was recovered from the solution and reprecipitated twice by the THF−hexane system. Yields of the star and the block copolymer were 88% (2.04 g) and 94% (0.92 g) yields, respectively. ^{1}H NMR ($CDCl_3$): δ 6.05−7.80 (broad, 1320H, ArH), 2.18−2.58 (broad, 360H, ArC*H*$_3$), 1.00−2.10 (broad, 868H, CH_2 and CH), 0.59−0.82 (broad, 18H, C*H*$_3$CH$_2$CH(C*H*$_3$)), −0.08−0.52 (broad, 1040H, Si(CH_3)$_3$).

(2) 6-Arm ABD$_2$E$_2$ Star-Branched Polymer. To a THF (7.13 mL) solution of PTMSSLi (1.12 g, $\bar{M}_n$(calcd) = 9680 g/mol, $\bar{M}_n$(NMR) = 12 700 g/mol, 0.0881 mmol), a THF (16.8 mL) solution of PS-D$_2$-PαMS (0.598 g, 0.0302 mmol) was added at −78 °C and allowed to react for 30 h. A THF (2.30 mL) solution of DPE (0.248 mmol) was introduced to the reaction system at −78 °C for 2 h, and a THF (5.90 mL) solution of LiBr (1.77 mmol) was added to the mixture. After 1 h, MPVSO (1.25 g, 7.53 mmol) in THF (12.5 mL) was added to polymerize at −78 °C for 24 h. The reaction was quenched with degassed methanol, and the polymer mixture was precipitated by adding a large amount of hexane. The polymer mixture was dissolved in 20 mL of THF, and 180 mL of hexane was then added. To the turbid solution, 150 mL of methanol was slowly added, and the objective star-branched polymer was nearly completely precipitated, while the block copolymer generated during the polymerization was remained in solution. The same workup gave the objective ABD$_2$E$_2$ star and the diblock copolymer in 85% (1.90 g) and 94% (0.69 g) yield, respectively. ^{1}H NMR ($CDCl_3$): δ 6.03−8.01 (broad, 1360H, ArH), 2.26−2.52 (broad, 381H, ArC*H*$_3$), 1.03−2.19 (broad, 723H, CH_2 and CH), 0.63−0.82 (broad, 24H, C*H*$_3$CH$_2$CH(C*H*$_3$)), −0.08 to −0.58 (broad, 1240H, α-CH_3 and Si(CH_3)$_3$).

(3) 7-Arm ABCD$_2$E$_2$ Star-Branched Polymer. To a THF (8.85 mL) solution of PTMSSLi (1.40 g, $\bar{M}_n$(calcd) = 10 000 g/mol, $\bar{M}_n$(NMR) = 8570 g/mol, 0.163 mmol) was added a THF (14.2 mL) solution of 3-arm core-functionalized PS−PαMS−PMOS star polymer with two DPE moieties (0.902 g, 0.0299 mmol) at −78 °C and allowed to react for 28 h. A THF (2.80 mL) solution of DPE (0.302 mmol) was introduced to the reaction system for 3 h. After addition of a THF (7.50 mL) solution of LiBr (2.25 mmol) to the mixture −78 °C for 1 h, MPVSO (1.61 g, 9.68 mmol) in THF (16.1 mL) was added to polymerize at −78 °C for 24 h. The reaction was then quenched with degassed methanol, and the polymer mixture was precipitated by adding a large amount of hexane. The reaction mixture was dissolved in 30 mL of THF and 300 mL of hexane was then added. To the turbid solution was slowly added 150 mL of methanol under stirring. The objective star-branched polymer was precipitated nearly completely, and the block copolymer was almost remained in the solution. The same workup gave the objective ABCD$_2$E$_2$ star and the diblock copolymer in 87% (1.75 g) and 96% (1.82 g) yield. ^{1}H NMR (CDCl$_3$): δ 6.02−7.79 (broad, 2400H, ArH), 3.61−3.94 (broad, 216H, OCH$_3$), 2.18−2.54 (broad, 685H, ArC*H*$_3$), 1.03−2.17 (broad, 1277H, CH$_2$ and CH), 0.61−0.79 (broad, 30H, C*H*$_3$CH$_2$CH(C*H*$_3$)), −0.11 to −0.56 (broad, 1210H, α-CH$_3$ and Si(CH$_3$)$_3$).

Thermal Degradation of Star-Branched Polymers. In a typical run, the sample AE$_2$ (30.0 mg) was added into a glass tube under nitrogen, and the tube was sealed under high-vacuum conditions. The tube was immersed into an oil bath thermostated at 150 °C for 1 h. After opening the tube, 12.5 mg of the degraded sample AE$_2$ was obtained as a dark brown powder. Other samples were subjected to thermolysis according to the same method.

Results and Discussion

Synthesis of Chain-Functionalized Polymers with Two DPE Moieties. Recently, we have developed a new methodology based on the iterative approach, by which well-defined asymmetric star-branched polymers are successively and systematically synthesized.[43−49] This methodology involves only two sets of reactions for the whole iterative synthetic sequences, namely, an addition reaction of living anionic polymer to DPE or a DPE-chain-functionalized polymer to link the two polymer chains and an in-situ introduction of the DPE moiety via the generated 1,1-diphenylalkyl anion by reacting with 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene (DBr). Since the two reactions proceed quantitatively, they can be repeated several times to afford a series of asymmetric star-branched polymers.[48]

We have herein synthesized three kinds of chain-functionalized polymers with two DPE moieties by the reaction of 3,5-bis(3-(4-(1-phenylethenyl)phenyl)propoxy)benzyl bromide (D$_2$-Br) instead of DBr with each of the intermediate polymer anions generated in the iterative methodology. These polymers are chain-end-functionalized polystyrene (PS) with two DPE moieties (PS-D$_2$), polystyrene-*block*-poly(α-methylstyrene) functionalized with two DPE moieties between two blocks (PS-D$_2$-PαMS), and 3-arm ABC star-branched polymer core-functionalized with two DPE moieties consisting of PS, poly(α-methylstyrene) (PαMS), and poly(4-methoxystyrene) (PMOS) segments, as illustrated in Scheme 1. They were used as precursor polymers for the synthesis of asymmetric star-branched polymers having two PA arms.

The PS-D$_2$ was synthesized by the reaction of D$_2$Br with PSLi end-capped with DPE. The SEC profile exhibited a sharp monomodal peak (Figure 1a). The PS-D$_2$-PαMS was obtained by the linking reaction of PS-D with a slight excess of PαMSLi, followed by treatment with D$_2$Br. In the SEC profile of the resulting mixture, two sharp distinct peaks corresponding to the linked polymer and the deactivated PαMSLi used in excess were observed (Figure 1b). The linking efficiency was quantitative on the basis of two peak areas. By fractional precipitation using cyclohexane/hexane (3/2, v/v), the objective polymer, PS-D$_2$-PαMS, isolated in 85% yield, was found to possess a sharp monomodal distribution (Figure 1c). The 3-arm ABC star-branched polymer core-functionalized with two DPE moieties was synthesized by the reaction of D$_2$Br with 3-arm star-branched polymer anion prepared from PS-D-PαMS and a slight excess of PMOSLi. In the SEC profile of the resultant mixture, two sharp peaks corresponding to the star polymer and the deactivated PMOSLi used in excess are observed, and the ratio of the two peak areas agrees well with the original feed ratios, indicating the quantitative linking efficiency (Figure 1d). The core-functionalized star-branched polymer with two DPE moieties could be isolated in 87% yield by fractional precipitation using toluene and methanol (Figure 1e). The results are summarized in Table 1.

It is obvious that the molecular weights of the resulting polymers agree well with those predicted and their distributions are extremely narrow ($\bar{M}_w/\bar{M}_n < 1.02$). The ^{1}H NMR spectra indicated that two DPE moieties were introduced into the polymers by comparing with two resonances at 5.40 and 0.5−0.8 ppm respectively assigned to methylene protons of the DPE moiety and methyl protons of the initiator fragment. The same spectra also exhibited composition ratios identical to their feed ratios.

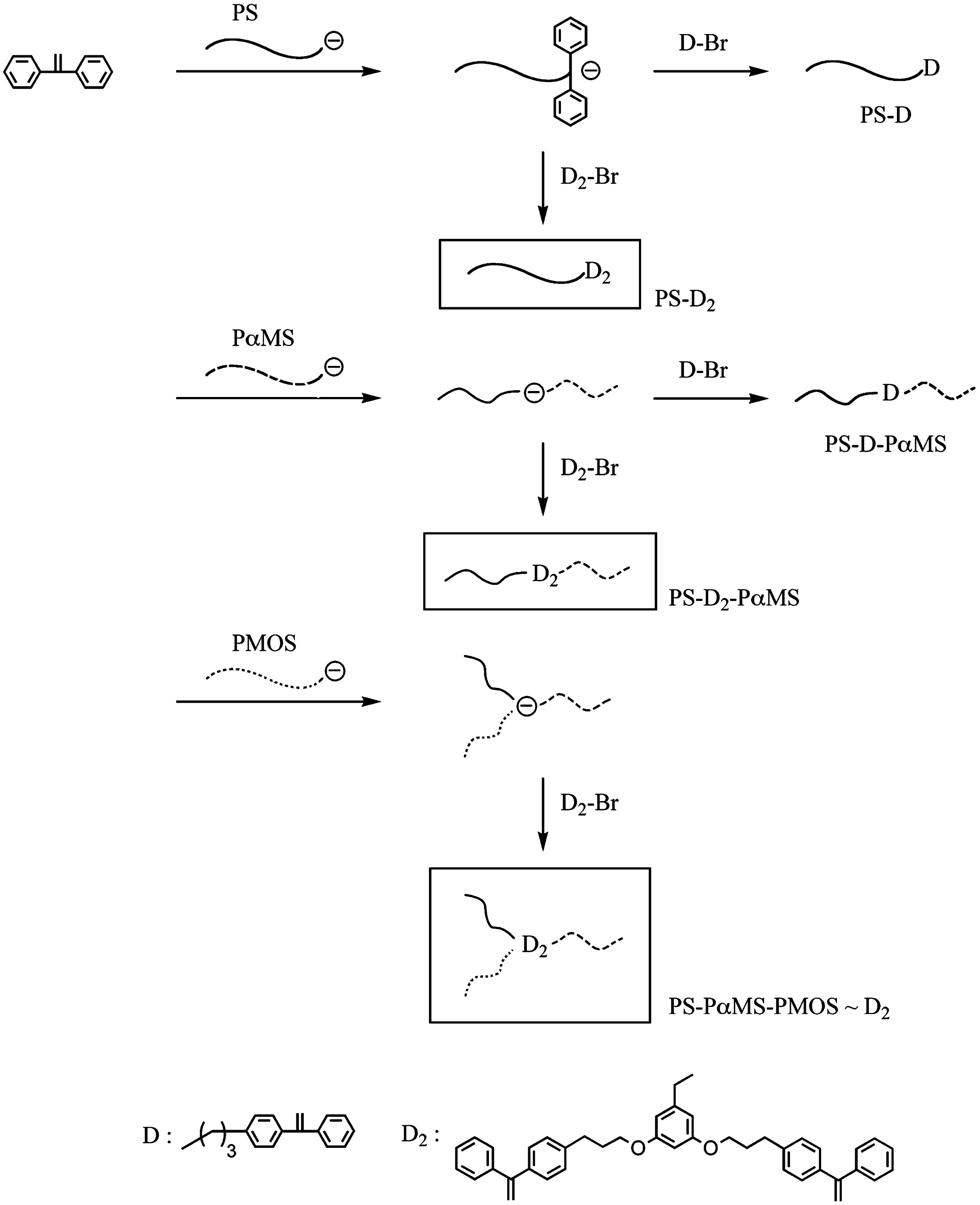
Branched Polymers Having Two Poly(4-methylphenylvinyl sulfoxide) (PMPVSO) Arms (First Series). In this section, the synthesis of 3-arm AE$_2$, 4-arm ABE$_2$, and 5-arm ABCE$_2$ asymmetric star-branched polymers having two PMPVSO (E) arms (the first series) is described. In these stars, other arms were PS (A), PαMS (B), and PMOS (C), respectively. As illustrated in Scheme 2, such star-branched polymers are synthesized by the addition reaction of *sec*-BuLi with two DPE moieties introduced into the precursor polymers, followed by the living anionic polymerization of 4-methylphenylvinyl sulfoxide (MPVSO) with the generated two 1,1-diphenylalkyl anions after the addition reaction.

In the synthesis, either of the chain-functionalized polymers with two DPE moieties was first reacted with an excess of *sec*-BuLi (1.9−2.5-fold excess) in order to be converted to the corresponding polymer anions. After the transformation, the unreacted *sec*-BuLi was capped with DPE and was altered to 3-methyl-1,1-diphenylpentyl anion. Then, the living anionic polymerization of MPVSO was subsequently conducted in THF at −78 °C for 24 h in the presence of a 10-fold or more excess of LiBr. Accordingly, MPVSO underwent the anionic polymerization not only with the two 1,1-diphenylalkyl anions in-situ generated in each precursor polymer (polymer anion) but also with 3-methyl-1,1-diphenylpentyl anion produced by capping the excess *sec*-BuLi, resulting in the formation of the objective star-branched polymer and MVPSO homopolymer (PMPVSO) in each case. The polymerizations were carefully quenched with degassed methanol, and the polymer mixtures were precipitated by adding a large amount of hexane. The polymer yields were quantitative in all cases by gravimetry. All of the star-branched polymers could be nearly quantitatively isolated from the polymer mixture by the selective precipitation in methanol in which PMPVSO homopolymer was completely soluble.

Figure 2a,c,e shows SEC profiles of the original reaction mixtures. In the synthesis of 3-arm AB$_2$ star-branched polymer, two peaks appeared significantly overlapped corresponding to the objective star and PMPVSO homopolymer formed as a byproduct. Only two distinct peaks were observed as well in the synthesis of 4-arm ABE$_2$ and 5-arm ABCE$_2$ stars. As mentioned above, the star-branched polymers were nearly quantitatively isolated by precipitation in methanol. As shown in Figure 2b,d,f, all of the isolated star-branched polymers exhibited symmetric sharp monomodal SEC distributions, their $\bar{M}_w/\bar{M}_n$ values being less than 1.04. The MPVSO homopolymer could be recovered in >90% yield in each case by evaporating the methanol solution, followed by precipitation in hexane. The homopolymers thus isolated also possess monomodal SEC distributions ($\bar{M}_w/\bar{M}_n < 1.12$), as shown in Figure 3a−c.

The characterization results of the isolated asymmetric star-branched polymers are summarized in Table 2. In this table, the calculated molecular weight ($\bar{M}_n$(calcd)) values and weight compositions of the stars were determined by their feed ratios and the assumption that two 1,1-diphenylalkyl anions in-situ generated in the precursor polymers and 3-methyl-1,1-diphe-

Scheme 1. Chain-Functionalized Polymers with Two DPE Moieties



nylpentyl anion possess the same initiating activity for the anionic polymerization of MPVSO to produce the polymers with the same molecular weight. The $\bar{M}_n$(NMR) values were determined from the ratios of integrated peak areas of the methyl protons of the initiator fragment (0.5−0.8 ppm), and each of the signals $\bar{M}_n$ characteristic of PS, PMPVSO, PaMS, and PMOS observed at 6.2−7.2 ppm (phenyl protons), 2.36 ppm (methyl protons), −0.1 to −0.45 ppm (methyl protons), and 3.72 ppm (methoxy protons), respectively. These ^{1}H NMR spectra are shown in Figure 4a−c. The absolute M_w values were measured by SLS.

It is obvious that in Table 2 the $\bar{M}_n$(calcd) values are in good agreement with those of $\bar{M}_n$(NMR) in all cases. The M_w(calcd) values also agreed with the M_w(SLS) ones. The weight compositions determined by ^{1}H NMR spectra are very similar to the values calculated from feed ratios. Surprisingly and interestingly, the total molecular weight of PMPVSO segment introduced into each star was found to be almost twice of the molecular weight of the recovered PMPVSO, as listed in Table 3.

Accordingly, all of the characterization results strongly support the above-mentioned assumption that two 1,1-diphenylalkyl anions generated in the precursor polymer and 3-methyl-1,1-diphenylpentyl anion possess the same initiating activity for the anionic polymerization of MPVSO to afford the polymers with the same chain length. Thus, the anionic polymerization of MPVSO proceeds in an ideal manner to give the expected 3-arm AE_2, 4-arm ABE_2, or 5-arm $ABCE_2$ asymmetric star-branched polymer having two PMPVSO arms. At the present

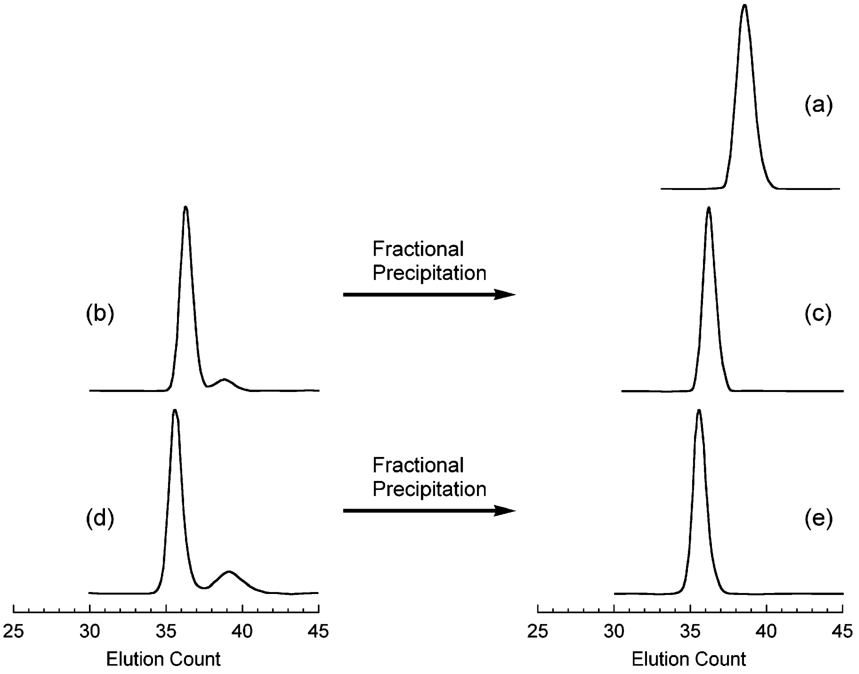


Figure 1. SEC profiles of PS-D_2 (a), PS-D_2-PαMS before (b) and after (c) fractional precipitaion, and 3-arm star-branched polymer (PS-PαMS-PMOS) core-functionalized with two DPE moieties before (d) and after fractional precipitation (e).

Table 1. Synthesis of Chain-Functionalized Polymers with Two DPE Moieties

	$\bar{M}_n$ (g/mol)			$\bar{M}_w$ (g/mol)				composition	
sample	calcd	SEC[a]	^{1}H NMR[b]	calcd	SLS[c]	$\bar{M}_w/\bar{M}_n$[a]	F[d]	calcd	^{1}H NMR[e]
PS-D_2	11 200	11 200	9 570			1.02	2.02	100	100
PS-D_2-PaMS[f]	20 200	20 400	19 800	20 400	20 000	1.01	2.00	47/53	46/54
PS−PaMS−PMOS-D_2[g]	30 100	27 500	30 100	30 400	32 100	1.01	2.02	32/34/34	32/34/34

[a] Estimated by SEC using polystyrene standards. [b] Determined by ^{1}H NMR. [c] Determined by SLS. [d] Functionality of DPE moieties determined by ^{1}H NMR. [e] PS, PS/PαMS, and PS/PαMS/PMOS determined by ^{1}H NMR, respectively. [f] End-functionalized polystyrene with DPE moiety (PS-D) used as a precursor polymer; $\bar{M}_n$(NMR) = 9460 g/mol, $\bar{M}_w/\bar{M}_n$= 1.02, functionality = 1.02. [g] In-chain-functionalized polystyrene-*block*-poly(α-methylstyrene) with DPE moiety (PS-D-PαMS) used as a precursor polymer; $\bar{M}_n$(NMR) = 20 100 g/mol, $\bar{M}_w/\bar{M}_n$= 1.01, functionality = 1.01.

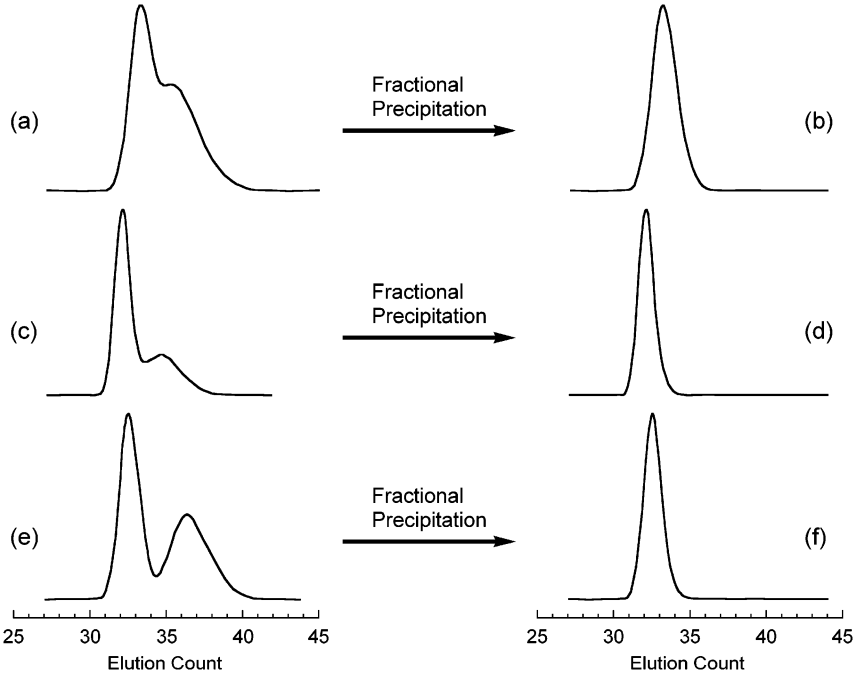


Figure 2. SEC profiles of 3-arm AE_2, 4-arm ABE_2, and 5-arm $ABCE_2$ star-branched polymers before (a, c, e) and after (b, d, f) fractional precipitation, respectively.

time, it is difficult to judge whether the two PMPVSO chains in each star are same in molecular weight.

5-Arm AD_2E_2, 6-Arm ABD_2E_2, and 7-Arm $ABCD_2E_2$ Asymmetric Star-Branched Polymers Having Two PMPVSO

Scheme 2. Synthesis of 3-Arm AE$_2$, 4-Arm ABE$_2$, and 5-Arm ABCE$_2$ Asymmetric Star-Branched Polymers

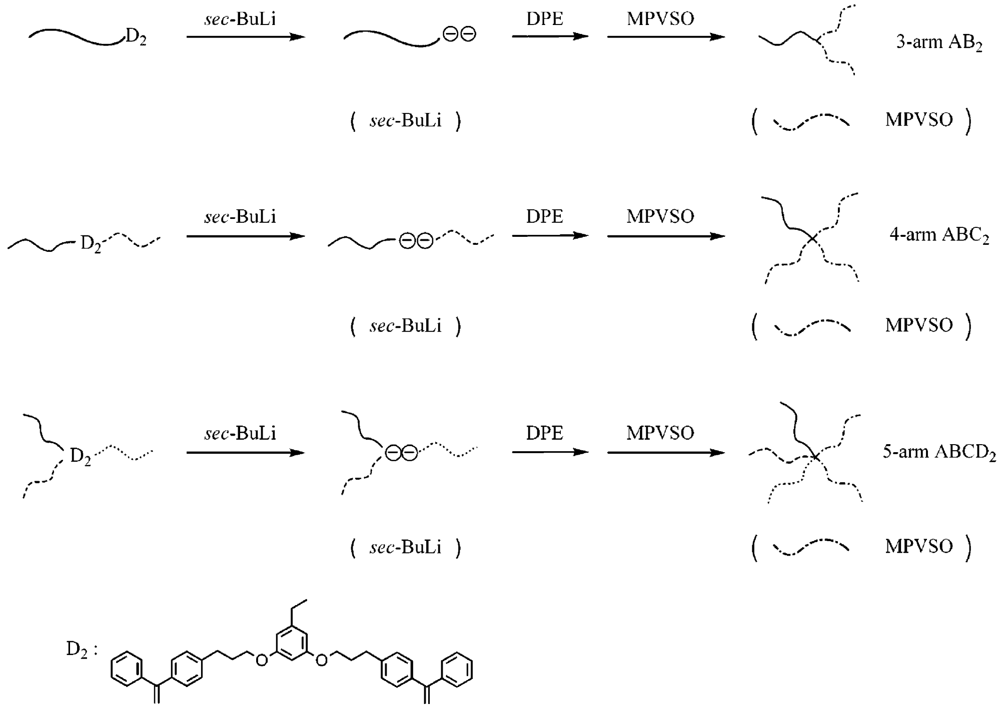


Table 2. Synthesis of 3-Arm AE$_2$, 4-Arm ABE$_2$, and 5-Arm ABCE$_2$ Asymmetric Star-Branched Polymers Having Two PMPVSO Arms

	$\bar{M}_n$ (g/mol)			$\bar{M}_w$ (g/mol)			composition	
star[a]	calcd	SEC[b]	^{1}H NMR[c]	calcd	SLS[d]	$\bar{M}_w/\bar{M}_n$[b]	calcd	^{1}H NMR[e]
AE$_2$	32 300	21 800	28 600	33 600	29 700	1.04	27/73	30/70
ABE$_2$	42 300	29 200	42 500	43 100	44 500	1.02	23/24/53	23/24/53
ABCE$_2$	51 000	27 200	52 700	52 500	54 300	1.03	21/19/19/41	21/18/18/43

[a] A: PS, B: PαMS, C: PMOS, and E: PMePVSO. [b] Estimated by SEC using polystyrene standards. [c] Determined by ^{1}H NMR. [d] Determined by SLS in THF at 25 °C; the d*n*/d*c* values are 0.167, 0.168, and 0.173 mL/g for AE$_2$, ABE$_2$, and ABCE$_2$ star-branched polymers, respectively. [e] A/E, A/B/E, and A/B/C/E determined by ^{1}H NMR.

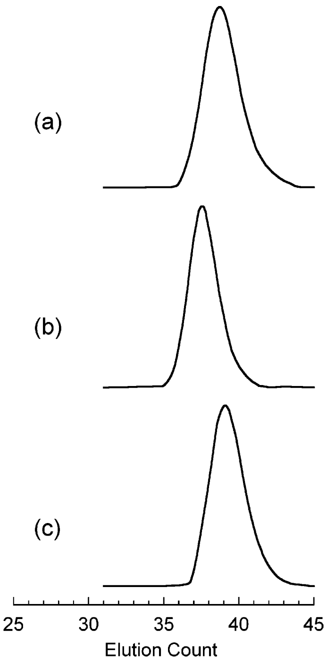


Figure 3. SEC profiles of MPVSO homopolymers recovered from the resulting mixtures of 3-arm AE$_2$ (a), 4-arm ABE$_2$ (b), and 5-arm ABCE$_2$ (c) star-branched polymers.

Arms (Second Series). The synthetic route for 5-arm AD$_2$E$_2$, 6-arm ABD$_2$E$_2$, and 7-arm ABCD$_2$E$_2$ asymmetric stars having two PMPVSO arms is illustrated in Scheme 3. As can be seen, the same two DPE-chain-functionalized polymers used in the synthesis of the first star series are employed as starting precursor polymers. Each precursor polymer was reacted with 2 equiv of poly(4-trimethylsilylstyryl)lithium (PTMSSLi) to link two PTMSS segments, followed by the living anionic polym-

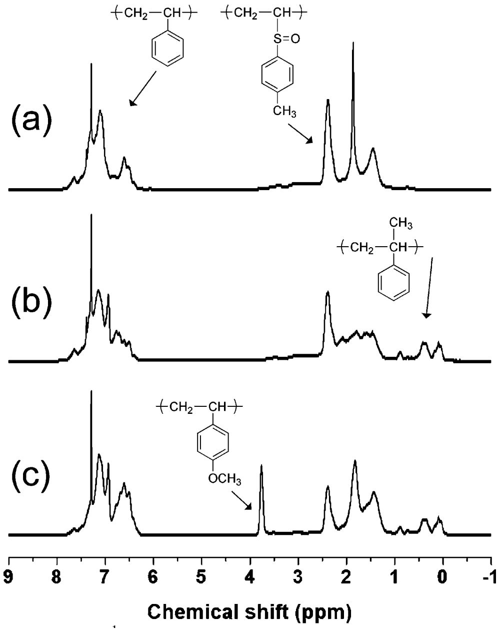


Figure 4. ^{1}H NMR spectra of 3-arm AE$_2$ (a), 4-arm ABE$_2$ (b), and 5-arm ABCE$_2$ (c) star-branched polymers.

Table 3. $\bar{M}_n$ Values of PMPVSO Recovered and PMPVSO Arms of 3-Arm AE_2, 4-Arm ABE_2, and 5-Arm $ABCE_2$ Stars

original sample	PMPVSO total $\bar{M}_n$ (in star) (g/mol)[a]	$\bar{M}_n$ (recovered) × 2 (g/mol)[b]	$\bar{M}_w/\bar{M}_n$[c]
AE_2	19 000	20 600 (10 300 × 2)	1.12
ABE_2	22 700	22 400 (11 200 × 2)	1.09
$ABCE_2$	22 600	20 800 (10 400 × 2)	1.09

[a] Total $\bar{M}_n$ value of two PMPVSO arms introduced into asymmetric star polymers determined by ^{1}H NMR. [b] Determined by ^{1}H NMR. [c] Determined by SEC using polystyrene standards.

erization of MPVSO with two 1,1-diphenylalkyl anions in-situ generated at the linking points, resulting in the introduction of two PMPVSO segments. As 1.5−2.3-fold excesses of PTMSSLi over the DPE moiety were used in the linking reaction, the excess unreacted PTMSSLi was end-capped with DPE to convert to the corresponding 1,1-diphenylalkyl anion prior to the anionic polymerization of MPVSO. Accordingly, in addition to the formation of the objective asymmetric star-branched polymers, undesirable diblock copolymers, poly(4-trimethylsilylstyrene)-*block*-poly(4-methylphenylvinyl sulfoxide) (PTMSS-*b*-PMPVSO), were by-produced in all cases.

As can be seen in Figure 5a,c,e, SEC profiles of the polymerization mixtures always exhibit two peaks corresponding to the objective stars and the block copolymers as byproducts. The asymmetric star-branched polymers all could be isolated in >85% yields by careful fractional precipitation using THF/hexane/methanol mixtures. The star-branched polymers thus isolated show sharp symmetrical monomodal SEC distributions, as shown in Figure 5b,d,f. The block copolymers were recovered in >80% yields from the solutions. They were found to exhibit as well monomodal SEC distributions as shown in Figure 6a−c. The results of the isolated asymmetric star-branched polymers and the recovered block copolymers are summarized in Tables 4 and 5.

Similar to the case of the first star series, the calculated molecular weights ($\bar{M}_n$(calcd)) and weight compositions of the stars were determined by their feed ratios and the assumption that two 1,1-diphenylalkyl anions in-situ generated at the core of the stars and chain-end 1,1-diphenylalkyl anions of the block copolymers possessed the same initiating activity for the anionic polymerization of MPVS to produce the polymers with the same molecular weights. The $\bar{M}_n$(NMR) values were calculated from the ratios of integrated peak areas of the methyl protons of the initiator fragment (0.5−0.8 ppm) and each of the signals characteristic of PS, PTMSS, PMPVSO, PaMS, and PMOS observed at 6.2−7.2 ppm (phenyl protons), 0.22 ppm (silylmethyl protons), 2.36 ppm (methyl protons), −0.1 to −0.45 ppm (methyl protons), and 3.72 ppm (methoxy protons), respectively. These ^{1}H NMR spectra are shown in Figure 7a−c. The absolute M_w values were measured by SLS.

As can be seen in Table 4, agreement between the $\bar{M}_n$(calcd) and $\bar{M}_n$(NMR) values is quite satisfactory in all cases. Moreover, the M_w(calcd) values are very close to those of M_w(SLS). It was observed that all of the stars possessed the weight compositions nearly equal to the values calculated from feed ratios. Again surprisingly, the total molecular weight of two PMPVSO segments in each star was comparable to twice the molecular weight of PMPVSO segment of the recovered block copolymer as listed in Table 5. Accordingly, the anionic polymerization of MPVSO appeared to proceed equally with two 1,1-diphenylalkyl anions in-situ generated at the core of the star and chain-end 1,1-diphenylpentyl anion of PTMSSLi to produce the polymers of MPVSO with the same chain length. Thus, all the characterization results strongly indicate that the resulting polymers are the expected and well-defined 5-arm AD_2E_2, 6-arm ABD_2E_2, and 7-arm $ABCD_2E_2$ asymmetric star-branched polymers with two PMPVSO arms.

Throughout the synthesis of asymmetric stars in this study, the anionic polymerization process of MPVSO initiated with different 1,1-diphenylalkyl anions and the uniformity of two PMPVSO segments introduced into the asymmetric stars may be a point of controversy. After the addition reaction, either 3-methyl-1,1-diphenylpentyl anion produced from the excess *sec*-BuLi or the chain-end 1,1-diphenylalkyl anion produced from the excess PTMSSLi is always present with two 1,1-diphenylalkyl anions generated in each precursor polymer in the same polymerization system, as shown in Schemes 2 and 3. One would reasonably presume that such 1,1-diphenylalkyl anions exhibit different initiating activity for the anionic polymerization of MPVSO. Furthermore, it may be speculated that even two PMPVSO segments initiated with the two 1,1-diphenylalkyl anions generated in each of the precursor polymers have distinct chain lengths due to the potential steric hindrance around the core. Nevertheless, the analytical results indicate that the anionic polymerization of MPVSO proceeds equally with all of the different 1,1-diphenylalkyl anions to afford the polymers with nearly the same chain length.

In order to elucidate the polymerization behavior, the resultant MPVSO homopolymer and PTMSS-*b*-PMPVSO diblock copolymer formed as byproducts were isolated and characterized. The results are summarized in Tables 3 and 5. As mentioned above, it was observed that the total chain length of two PMPVSO segments in each star was very close to double value of either MPVSO homopolymer or PMPVSO segment of PTMSS-*b*-PMPVSO diblock copolymer obtained in the same polymerization system. Taking into consideration of such an anionic polymerization behavior of MPVSO, it is suggested that the two PMPVSO chains introduced into each of the stars are same or very similar in molecular weight, although there still remains a question on the uniformity of the two PMPVSO segments. This surprising phenomenon may possibly be attributed to the significant reduced reactivities of the different 1,1-diphenylalkyl anions as well as the propagating chain-end anions by the presence of a 10-fold or more excess of LiBr. Whatever the reason, the chain length of PMPVSO arm in asymmetric stars can be adjusted by the control of feed ratios of MPVSO to *sec*-BuLi or PTMSSLi. In other words, it is possible to synthesize well-defined and precisely controlled asymmetric star-branched polymers having two PMPVSO arms even by using either *sec*-BuLi or PTMSSLi in excess in the linking reaction. An additional advantageous point for this is the easy separation of the objective asymmetric star-branched polymers from their byproduct polymers as mentioned above. If *sec*-BuLi or PTMSSLi was not used in excess in the linking reaction, the resulting asymmetric stars always involve their precursor polymers leading to difficult separation.

Thermal Treatment of Star-Branched Polymers: Conversion of PMPVSO Segment to Polyacetylene (PA) Chain. Figure 8a−f shows thermogravimetric (TGA) curves of the asymmetric star-branched polymers having PMPVSO arms synthesized in this study. The first characteristic transitions at around 200 °C may be ascribed to the elimination of 4-methylphenylsulfenic acid from PMPVSO segments in all samples. The weight losses at the temperatures in the range from 150 to 250 °C were nearly consistent with those risen by complete elimination. FT-IR spectra of the original stars always showed a strong absorption band at 1045 cm^{-1} corresponding to the

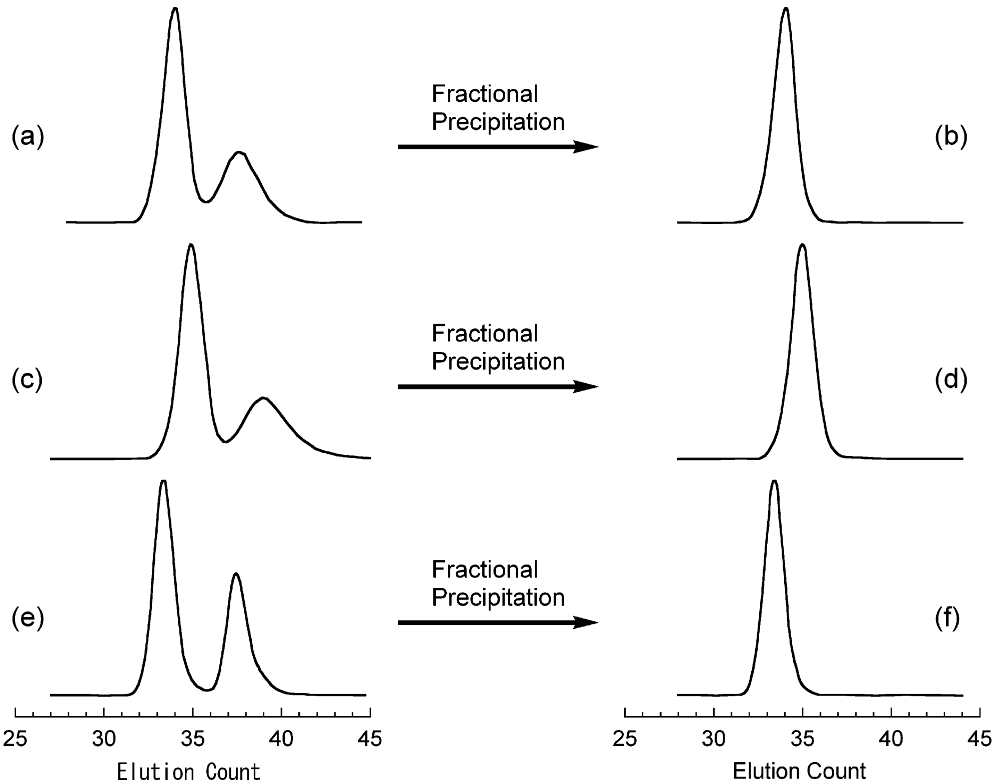
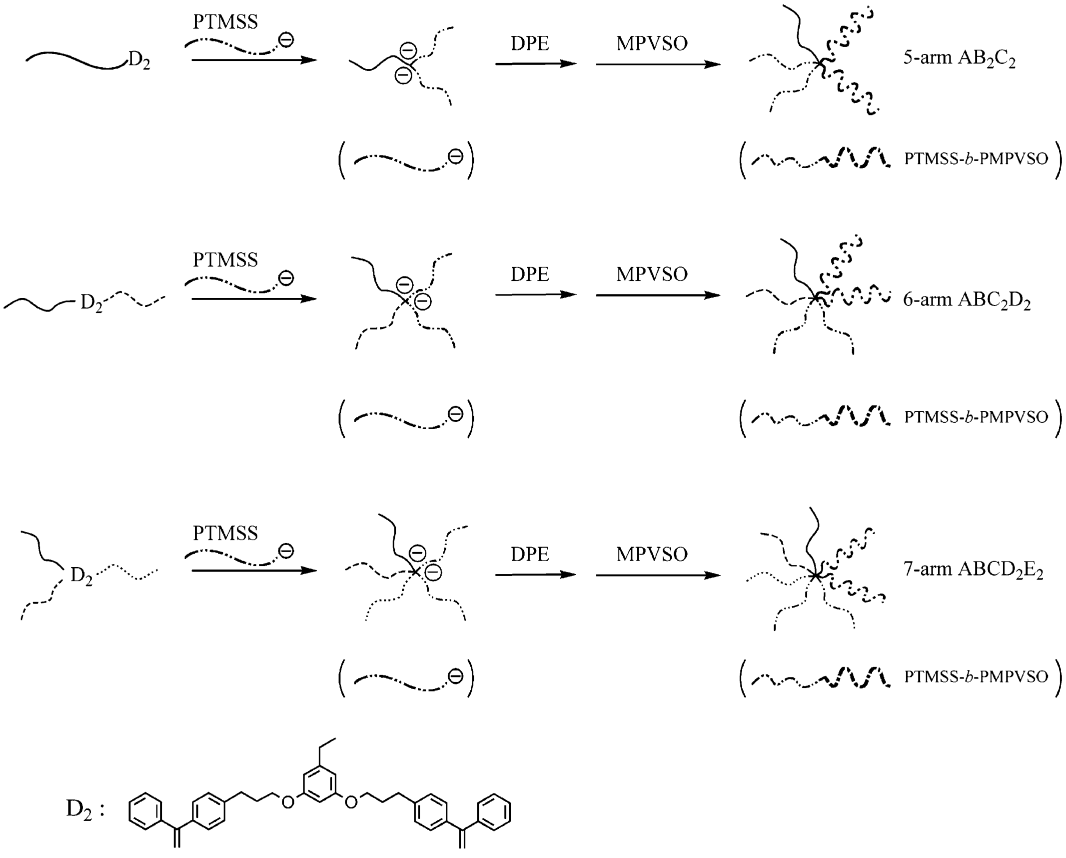


Figure 5. SEC profiles of 5-arm AD_2E_2, 6-arm ABD_2E_2, and 7-arm $ABCD_2E_2$ star-branched polymers before (a, c, e) and after (b, d, f) fractional precipitation, respectively.

Scheme 3. Synthesis of 5-Arm AD_2E_2, 6-Arm ABD_2E_2, and 7-Arm $ABCD_2E_2$ Asymmetric Star-Branched Polymers



S=O stretching. This band completely disappeared after thermal treatment in each sample. Typically, IR spectra of the AE_2 star before and after thermal treatment are shown in Figure 9a,b. It was observed from elemental analysis of the resulting samples that sulfur was almost absent in all cases. These analytical results clearly confirmed the complete conversion to PA chains by quantitatively eliminating 4-methylphenylsulfenic acid from two PMPVSO segments in the original star-branched polymers. The

Table 4. Synthesis of 5-Arm AD_2E_2, 6-Arm ABD_2E_2, and 7-Arm $ABCD_2E_2$ Asymmetric Star-Branched Polymers Having Two PMPVSO Arms

	$\bar{M}_n$ (g/mol)			$\bar{M}_w$ (g/mol)			composition	
star[a]	calcd	SEC[b]	^{1}H NMR[c]	calcd	SLS[d]	$\bar{M}_w/\bar{M}_n$[b]	calcd	^{1}H NMR[e]
AD_2E_2	50 000	30 800	45 800	51 500	52 800	1.03	17/41/42	19/37/44
ABD_2E_2	60 800	40 500	58 000	62 600	63 400	1.03	17/16/32/35	18/17/43/22
$ABCD_2E_2$	73 400	47 200	69 800	75 600	75 900	1.03	16/13/13/27/31	15/14/14/25/32

[a] A: PS, B: PαMS, C: PMOS, D: PTMSS, and E: PMPVSO. [b] Estimated by SEC using polystyrene standards. [c] Determined by ^{1}H NMR. [d] Determined by SLS in THF at 25 °C; the d*n*/d*c* values are 0.173, 0.170, and 0.174 (mL/g) for AB_2C_2, ABC_2D_2, and $ABCD_2E_2$ star-branched polymers, respectively. [e] A/D/E, A/B/D/E, and A/B/C/D/E determined by ^{1}H NMR.

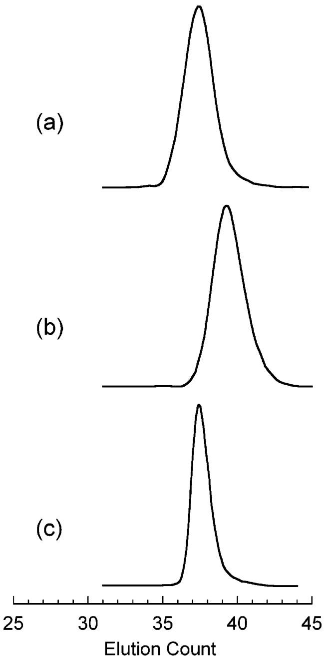


Figure 6. SEC profiles of (PTMSS-*block*-PMPVSO)s recovered from the resulting mixtures of 5-arm AD_2E_2 (a), 6-arm ABD_2E_2 (b), and 7-arm $ABCD_2E_2$ (c) star-branched polymers.

Table 5. $\bar{M}_n$ Values of PMPVSO Segment of Block Copolymers and PMPVSO Arms of 5-Arm AD_2E_2, 6-Arm ABD_2E_2, and 7-Arm $ABCD_2E_2$ Stars

	PMPVSO		
original sample	total $\bar{M}_n$ (in star) (g/mol)[a]	$\bar{M}_n$ (in block copolymer) × 2 (g/mol)[b]	$\bar{M}_w/\bar{M}_n$[c]
AD_2E_2	16 400	20 600 (10 300 × 2)	1.08
ABD_2E_2	19 000	20 400 (10 200 × 2)	1.09
$ABCD_2E_2$	19 900	21 600 (10 800 × 2)	1.04

[a] Total $\bar{M}_n$ values of two PMPVSO arms introduced into star determined by ^{1}H NMR. [b] Determined by ^{1}H NMR. [c] Determined by SEC using polystyrene standards.

resulting star-branched polymers having two PA arms were insoluble but swollen in most of the organic solvents.

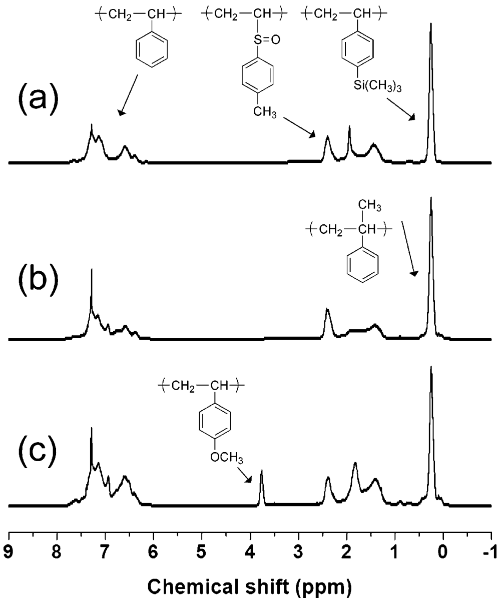


Figure 7. ^{1}H NMR spectra of 5-arm AD_2E_2 (a), 6-arm ABD_2E_2 (b), and 7-arm $ABCD_2E_2$ (c) star-branched polymers.

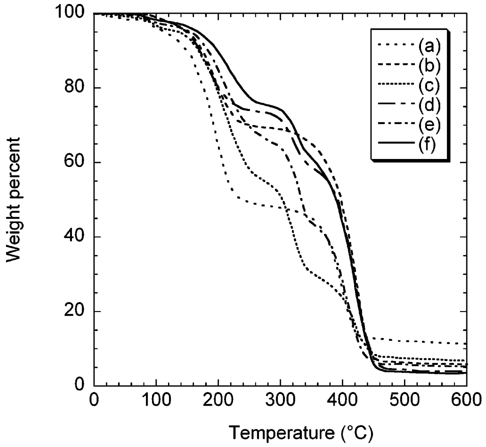


Figure 8. TGA curves of 3-arm AE_2 (a), 4-arm ABE_2 (b), 5-arm $ABCE_2$ (c), 5-arm AD_2E_2 (d), 6-arm ABD_2E_2 (e), and 7-arm $ABCD_2E_2$ (f) star-branched polymers.

Conclusions

Two series of new 3-arm AE_2, 4-arm ABE_2, 5-arm $ABCE_2$, and 5-arm AD_2E_2, 6-arm ABD_2E_2, 7-arm $ABCD_2E_2$ asymmetric star-branched polymers having two PMPVSO arms have been synthesized by the addition reaction of either *sec*-BuLi or PTMSSLi with two DPE-chain-functionalized polymers, followed by the living anionic polymerization of MPVSO with the 1,1-diphenylalkyl anions in-situ generated by the addition reaction. The target star-branched polymers could be isolated in more than 85% yields by fractional precipitation in all cases. The isolated stars all possessed the expected structures with well-defined branched architectures and precisely controlled chain lengths and compositions as confirmed by the characterizations with ^{1}H NMR, SEC, and SLS. Surprisingly and interestingly, the total molecular weight of two PMPVSO arms in the star was nearly doubled to the molecular weight of either the MPVSO homopolymer or the PMPVSO segment of the block copolymer formed as byproduct in each case. Additionally, the star-branched polymers synthesized could be completely converted to novel functional asymmetric stars having two rigid PA arms by thermal treatment. Morphological behaviors of such star polymers are in progress and will be reported in the near future.

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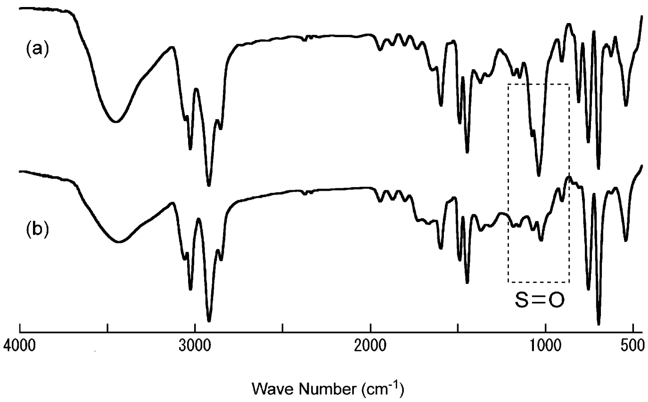

Figure 9. FT-IR spectra of AE_2 star-branched polymers before (a) and after (b) thermal treatment.

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