

SYNTHESIS OF HETEROARM STAR POLYMERS COMPRISING POLY(4-METHYLPHENYL VINYL SULFOXIDE) SEGMENT BY LIVING ANIONIC POLYMERIZATION*

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Abstract A series of 3-arm ABC and AA'B and 4-arm ABCD, AA'BC and AA'A''B heteroarm star polymers comprising one poly(4-methylphenyl vinyl sulfoxide) segment and other segments such as polystyrene, poly(α -methylstyrene), poly(4-methoxystyrene) and poly(4-trimethylsilylstyrene) were synthesized by living anionic polymerization based on diphenylethylene (DPE) chemistry. The DPE-functionalized polymers were synthesized by iterative methodology, and the objective star polymers were prepared by two distinct methodologies based on anionic polymerization using DPE-functionalized polymers. The first methodology involves an addition reaction of living anionic polymer with excess DPE-functionalized polymer and a subsequent living anionic polymerization of 4-methylphenyl vinyl sulfoxide (MePVSO) initiated from the *in situ* formed polymer anion with two or three polymer segments. The second methodology comprises an addition reaction of DPE-functionalized polymer with excess *sec*-BuLi and a following anionic polymerization of MePVSO initiated from the *in situ* formed polymer anion and 3-methyl-1,1-diphenylpentyl anion as well. Both approaches could afford the target heteroarm star polymers with predetermined molecular weight, narrow molecular weight distribution ($M_w/M_n < 1.03$) and desired composition, evidenced by SEC, ¹H-NMR and SLS analyses. These polymers can be used as model polymers to investigate structure-property relationships in heteroarm star polymers.

Keywords: Star polymer; Anionic polymerization; Macromonomer; DPE chemistry.

INTRODUCTION

The construction of polymer materials with controlled compositions, topologies and functionalities has been the enduring focus in polymer science^[1–5]. Among them, heteroarm star polymers with different arm segments have attracted much attention since they can form more complex morphologies due to their heterophase structure and chain-branching architecture^[6–16]. To date, many ABC star polymers have been successfully synthesized, however, reports on synthesis of well-defined ABCD and ABCDE star polymers are scarce due to the difficulty in synthesis^[17–26]. The 1,1-diphenylethylene (DPE) chemistry has proven to be a promising approach to heteroarm star polymers with various segments up to seven chemical compositions^[19–22].

As well-known soluble precursors to polyacetylene, poly(phenyl vinyl sulfoxide) (PPVSO) and its derivatives have been successfully synthesized by anionic polymerization^[27–30], and their block copolymers were also synthesized by sequential anionic polymerization^[31, 32]. The thermally labile segment could be converted to

* This work was financially supported by the National Natural Science Foundation of China (Nos. 20844001 and 20874067), the Key Project of Chinese Ministry of Education (No. 209049), and Natural Science Fund for Colleges and Universities of Jiangsu Province (No. 08KJB150015).

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Received November 9, 2009; Revised December 21, 2009; Accepted December 25, 2009

doi: 10.1007/s10118-010-9166-y

polyacetylene (PA) by thermal treatment, and the resultant block copolymers comprising PA segment can phase-separate at molecular level and self-organize to form supramolecular-ordered nanostructures^[32–34]. However, the reports on synthesis and properties of well-defined star polymers with conductive PA segment or its precursors are very limited until now^[19, 20]. To synthesize star polymers comprising conductive PA precursors, a more stable PPVSO derivative poly(4-methylphenyl vinyl sulfoxide) (PMePVSO) was designed and synthesized in our previous study, and novel heteroarm star polymers with one or two PMePVSO segment(s) and chemical compositions up to 5 such as ABCDE and ABCD₂E₂ stars were successfully prepared by living anionic polymerization^[19, 20].

When the polarity of various segments is different, heteroarm star polymers are expected to exhibit unique microphase-separated suprastructures which are relative to chemical compositions, chain length of each segment and arm number. To further understand the structure-property relationships in heteroarm star polymers, various types of star polymers comprising PSt, PMePVSO and/ or other segments were synthesized as model polymers in this study. To this end, two distinct methodologies based on living anionic polymerization using DPE-functionalized polymers were used to synthesize 3-arm ABC and AA'B and 4-arm ABCD, AA'BC and AA'A'B star polymers, and a series of heteroarm star polymers comprising one PMePVSO segment were obtained after fractional precipitation. This study is primarily focused on the synthesis, and the properties of various stars will be investigated in our following research.

EXPERIMENTAL

Materials

Most of the reagents (> 98% purities) were purchased from Aldrich. 1-(4-(3-Bromopropyl)phenyl)-1-phenylethylene (DBr), 4-methylphenyl vinyl sulfoxide (MePVSO), DPE-functionalized polymers and 4-trimethylsilylstyrene (TMSS) were synthesized and purified as previously reported^[19, 35]. Lithium bromide (LiBr) was dried at 110°C overnight under high vacuum conditions. Styrene (St), α -methylstyrene (α MS) and 4-methoxystyrene (MOS) were washed with 10% NaOH aqueous solution, dried over MgSO₄ and distilled over Bu₂Mg under reduced pressure. The monomers were finally distilled over Bu₂Mg on the vacuum line into ampoules equipped with break-seals that were prewashed with potassium naphthalenide in THF.

Synthesis of DPE-Functionalized Polymers with One DPE Moiety by Iterative Methodology Using DBr

The synthesis of polystyrene-poly(α -methylstyrene) diblock copolymer (PS-D-P α MS) was taken as an example^[19]. To a solution of P α MSLi (2.06 g, 0.210 mmol, M_n (SEC) = 9800) in THF (23.9 mL) was added a solution of PS-D (1.90 g, 0.198 mmol) in THF (20.5 mL) at –78°C and the mixture was allowed to stand for 2 h. After adding a solution of DPE (0.250 mmol) in THF (2.17 mL), the mixture was reacted with DBr (0.324 mmol) prepurified with Bu₂Mg (0.102 mmol) for 1 h at room temperature. After 10 min, the resulting polymer was poured into a large amount of methanol. The DPE-in-chain-functionalized PS-D-P α MS was isolated in 88% yield (3.50 g) by fractional precipitation using hexane and cyclohexane: M_n (SEC) = 19700, M_w/M_n = 1.01. Other DPE-end-functionalized polystyrene (PS-D), DPE-in-chain-functionalized polystyrene (PS-D-PS'), PS-D-PMOS and PS-D-PTMSS diblock copolymers and DPE-core-functionalized PS-P α MS-PMOS star were synthesized and purified according to similar methods.

Synthesis of Heteroarm Star Polymers by Anionic Polymerization Using Excess DPE-Functionalized Polymers

In a typical polymerization, to a solution of poly(α -methylstyryl)lithium (0.430 g, 0.0442 mmol) was added a solution of PS-D-PS' (1.11 g, 0.0566 mmol) in THF (15.4 mL) at –78°C and the mixture was allowed to stand for 24 h. A solution of LiBr (0.906 mmol) in THF (3.00 mL) was then added to the mixture. After 10 min, MePVSO (0.460 g, 2.77 mmol) in THF (4.22 mL) was introduced into the reaction system to be polymerized at –78°C for 24 h. After polymerization, the living anionic polymer was quenched by degassed methanol and recovered by precipitation into a large amount of hexane. The polymer mixture was dissolved into 20 mL of THF, and then 80 mL of hexane was added. The precipitated polymer was recovered by filtration. After

purification by precipitating the polymer twice from THF into methanol and freeze-drying with benzene for 12 h, the target 4-arm PS-PS'-P α MS-PMePVSO star polymer (S3) was isolated in 88% yield (1.58 g): $M_n(\text{SEC}) = 33000$, $M_w/M_n = 1.02$. Other AA'B (S1), AA'A''B (S2) and AA'BC (S4 and S5) star polymers were synthesized according to a similar approach, and the reaction time to form polymer anion with two and three polymer segments was also 24 h. These polymers were purified by fractional precipitation as described as follows.

PS-PS'-PMePVSO star (S1): The polymer was isolated in 85% yield by fractional precipitation using THF/cyclohexane/hexane (1:10:2, $V/V/V$). $M_n(\text{SEC}) = 23700$, $M_w/M_n = 1.03$.

PS-PS'-PS''-PMePVSO star (S2): The polymer was isolated in 87% yield by fractional precipitation using THF/cyclohexane/hexane (1:10:4, $V/V/V$). $M_n(\text{SEC}) = 31300$, $M_w/M_n = 1.03$.

PS-PS'-PTMSS-PMePVSO star (S4): The polymer was isolated in 85% yield by fractional precipitation using THF/hexane/methanol (1:2:3, $V/V/V$). $M_n(\text{SEC}) = 32300$, $M_w/M_n = 1.03$.

PS-PS'-PMOS-PMePVSO star (S5): The polymer was isolated in 86% yield by fractional precipitation using THF/cyclohexane/methanol (1:15:5, $V/V/V$). $M_n(\text{SEC}) = 31800$, $M_w/M_n = 1.02$.

Synthesis of Heteroarm Star Polymers by Anionic Polymerization Using DPE-Functionalized Polymers in the Presence of Excess *sec*-BuLi

In a typical run, to a heptane (1.50 mL) solution of *sec*-butyllithium (*sec*-BuLi) (0.0612 mmol) was added a THF (7.17 mL) solution of PS-D-P α MS (0.663 g, 0.0335 mmol) at -78°C and the mixture was allowed to stand for 4 h. A THF (2.24 mL) solution of DPE (0.124 mmol) was introduced to the reaction system at -78°C for 1 h to cap the excess *sec*-BuLi and then a THF (5.00 mL) solution of LiBr (1.51 mmol) was added to the mixture. After 30 min, MePVSO (0.636 g, 3.83 mmol) in THF (5.83 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 PS-P α MS-PMePVSO star polymer (S6) was wholly precipitated, while the PMPVSO homopolymer remained in the solution. After freeze-drying with dry benzene, 3-arm ABC star polymer was obtained almost quantitatively: $M_n(\text{SEC}) = 23600$, $M_w/M_n = 1.02$. The PMePVSO homopolymer was recovered in quantitative yield by evaporating the methanol solution, followed by precipitation in hexane: $M_n(\text{SEC}) = 8330$, $M_w/M_n = 1.09$. Other ABC and ABCD star polymers were synthesized according to a similar procedure by using various DPE-functionalized polymers as macromonomers.

Characterization

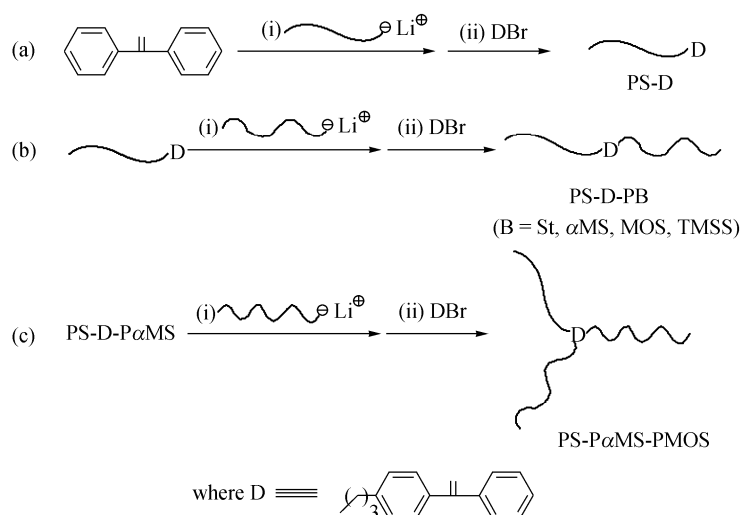
All ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded in CDCl_3 on a Bruker DPX spectrometer. Size exclusion chromatography (SEC) was performed on a Tosoh HLC 8020 instrument with UV (254 nm) and refractive index detection. THF was used as eluent with a flowing rate of 1.0 mL/min at 40°C , and polystyrene standards were used as calibrations. Static light scattering (SLS) measurements were performed on an Ohotsuka Electronics DLS-7000 instrument equipped with a He-Ne laser (633 nm) in THF at 25°C . The refractive index increment (dn/dc) in THF at 25°C was determined with an Ohotsuka Electronics DRM-1020 refractometer operating at 633 nm.

RESULTS AND DISCUSSION

Successive Synthesis of DPE-Functionalized Polymers by Iterative Methodology Using DBr

The methodology based on living anionic polymerization using 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene (DBr) as a core reagent was used to synthesize DPE-functionalized polymers. It involves two sets of quantitative reactions for the whole iterative synthetic sequences, namely, the addition reaction of living anionic polymer to DPE or DPE-functionalized polymer followed by the *in situ* reaction of the resultant 1,1-diphenylalkyl anion with the DPE derivative to introduce the DPE functionality (Scheme 1). Thus, DPE-chain-end-functionalized polystyrene (A, PS-D), DPE-in-chain-functionalized PS-P α MS diblock copolymer (AB, A = PS, B = P α MS, PMOS or PTMSS) and polystyrene (AA', PS-D-PS'), and DPE-core-functionalized 3-arm PS-P α MS-PMOS star

polymer (ABC) were obtained, and the polymerization results are listed in Table 1. It can be seen the molecular weights of DPE-functionalized polymers determined by $^1\text{H-NMR}$ agreed well with the predicted values, and the molecular weight distribution was narrow. In all cases, the degree of DPE-functionality (F) was determined to be quantitative by $^1\text{H-NMR}$ using two resonances at $\delta = 5.40$ and $0.5\text{--}0.8$ which were assigned to methylene protons in the DPE moiety and methyl protons of the initiator fragment.



Scheme 1 Successive synthesis of chain-end-functionalized PS (A), in-chain-functionalized PS-P α MS, PS-PMOS and PS-PTMSS diblock copolymers (AB) and PS-D-PS (AA'), and core-functionalized 3-arm PS-P α MS-PMOS (ABC) star polymer with one DPE moiety

Table 1. Synthesis of PS-D (A), PS-D-P α MS (AB₁), PS-D-PMOS (AB₂), PS-D-PTMSS (AB₃), PS-D-PS (AA') and 3-arm PS-P α MS-PMOS (ABC) star polymer with one DPE moiety

Type	$M_n(\text{calcd})$	$M_n(\text{SEC})^a$	M_w/M_n^a	$M_n(\text{NMR})^b$	M_w	F^c	$C(\text{calcd})^d$	$C(\text{NMR})^e$
A	9800	9600	1.02	9600	9800 ^f	1.02	100	100
AB ₁	19600	19700	1.01	19800	20000 ^f	1.02	49/51	48/52
AB ₂	20000	19500	1.02	20000	20400 ^f	1.01	48/52	48/52
AB ₃	19700	19200	1.02	19600	20000 ^f	1.02	49/51	49/51
AA'	19800	19600	1.01	19600	19800 ^f	1.01	48/52	49/51
ABC	31000	27500	1.01	31500	32100 ^g	1.01	31/33/36	30/32/38

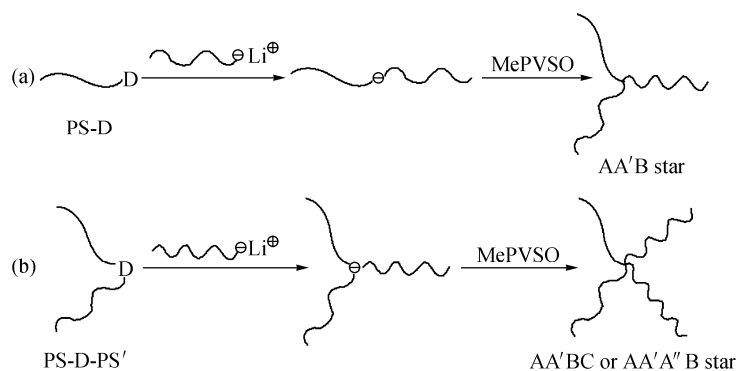
^a Determined by SEC; ^b Determined by $^1\text{H-NMR}$; ^c DPE-functionality determined by $^1\text{H-NMR}$;

^d Weight composition of A, A/B, and A/B/C calculated from feed ratios, where A was PS, C was PMOS, and B₁ B₂ and B₃ were P α MS, PMOS and PTMSS, respectively; ^e Weight composition of various DPE-functionalized polymers determined by $^1\text{H-NMR}$; ^f Calculated from $M_n(\text{NMR})$ and $M_w/M_n(\text{SEC})$; ^g Determined by SLS in THF at 25°C, $dn/dc = 0.182$

Synthesis of AA'B, AA'A'B and AA'BC Heteroarm Star Polymers by Anionic Polymerization Using Excess DPE-Functionalized Polymers

It is obvious that heteroarm star polymers containing PMePVSO segment can't be effectively achieved by the above mentioned iterative methodology due to the low reactivity of the PMePVSO polymer anion with DPE moiety. In our previous study, an alternative methodology first developed by Fujimoto and coworkers^[6] was successfully used to prepare heteroarm star polymers comprising PMePVSO and other segments such as PS, P α MS, PMOS and PTMSS^[19]. This methodology involves two reactions, namely, (a) the living linking reaction of DPE-functionalized polymer as a macromonomer with insufficient living anionic polymer, and followed by (b) living anionic polymerization of a second monomer initiated from the *in situ* formed 1,1-diphenylalkyl anion. In this study, this versatile methodology was further generalized to synthesize AA'B, AA'A'B and AA'BC star

polymers (Scheme 2).



Scheme 2 Synthesis of AA'B, AA'A''B and AA'BC heteroarm star polymers by living anionic polymerization using excess DPE-functionalized polymers

The 3-arm AA'B and 4-arm AA'A''B and AA'BC stars containing one PMePVSO segment and two or three PS segments were synthesized by anionic polymerization of MePVSO using about 20–25-fold excess of LiBr additive initiated from the polymer anion with two different segments in THF at -78°C . The polymer anion was formed by reacting living anionic polymer with excess of PS-D (A) or PS-D-PS' (AA') in THF at -78°C , and the coupling reaction was conducted for 24 h to reach quantitative efficiency. After addition of a solution of LiBr in THF, the *in situ* anionic polymerization of MePVSO was performed in THF at -78°C for 24 h. After polymerization, the reaction mixtures were quantitatively obtained, and the target star polymers were isolated in yield beyond 85% by fractional precipitation. The polymerization results are shown in Table 2.

Table 2. Synthesis of 3-arm AA'B (S1) and 4-arm AA'A''B (S2) and AA'BC (S3–S5) star polymers by anionic polymerization of MePVSO initiated from *in situ* formed polymer anion with two or three segments in THF at -78°C

Sample ^a	M_n			M_w		M_w/M_n^b	Composition	
	Calcd	SEC ^b	¹ H-NMR ^c	Calcd	SLS ^d		Calcd ^e	¹ H-NMR ^f
S1	30800	23700	32100	31700	33500	1.03	65/35	63/37
S2	41200	31300	42200	42400	43900	1.03	72/28	71/29
S3	39700	33000	40600	40500	41800	1.02	49/27/24	48/28/24
S4	40100	32300	41400	41300	42700	1.03	49/26/25	48/28/24
S5	41300	31800	41200	42100	42000	1.02	47/26/27	48/26/26

^a S1–S5: where A was PS, B was PMePVSO, and C was PαMS (S3), PTMSS (S4) and PMOS (S5); ^b Estimated by SEC; ^c Determined by ¹H-NMR; ^d Determined by SLS, and the dn/dc values of samples S1 to S5 were 0.179, 0.180, 0.176, 0.173 and 0.174 mL/g, respectively; ^e Theoretical weight composition of A/B (S1 and S2) and A/B/C (S3–S5) of various stars; ^f Weight composition determined by ¹H-NMR

The high purity of DPE-functionalized polymer and LiBr is crucial for the synthesis of well-defined asymmetric star polymers. In the course of coupling reaction and polymerization, the existence of some impurities such as water in DPE-functionalized polymer and LiBr will deactivate part of the living polymer anion, accordingly the polymerization will lose control on molecular weight and chemical composition of various segments. Moreover, the existence of deactivated polymer will make the isolation of the target polymer more difficult. For reaction mixtures and the isolated star polymers in the synthesis of various stars, the SEC profiles are shown in Fig. 1. As can be seen, only two sharp peaks were observed in SEC profiles of the original polymer mixtures. The peak in high-molecular-weight side was corresponding to the target star polymer, and the another peak could be assigned to PS-D or PS-D-PS' used in excess and the possibly deactivated living anionic polymer. The ratios of the two peak areas were very close to those calculated from the feed ratios, suggesting the deactivated anionic polymer was very limited. After fractional precipitation using mixtures of THF, hexane and

cyclohexane, the target AA'B (S1), AA'A''B (S2) and AA'BC (S3–S5) were obtained. The SEC profiles of the isolated polymers in Fig. 1 exhibited symmetric monomodal distribution without any tail or shoulder, with M_w/M_n values being less than 1.03, indicating no significant side reactions during polymerization.

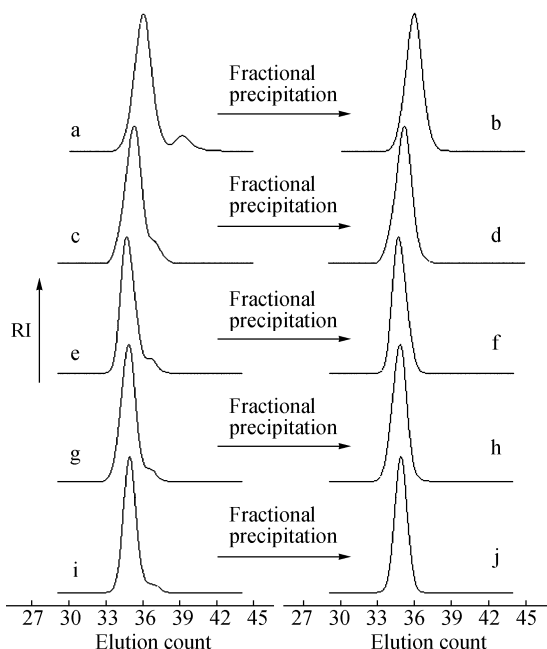


Fig. 1 SEC profiles of the resulting reaction mixtures and the isolated AA'B (S1), AA'A''B (S2) and AA'BC (S3–S5) star polymers: S1 (a, b), S2 (c, d), S3 (e, f), S4 (g, h) and S5 (i, j)

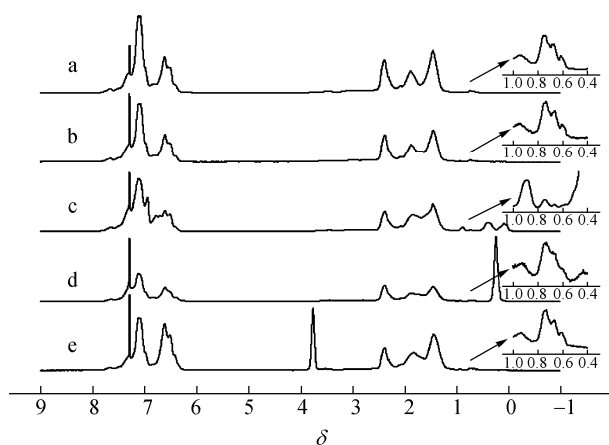


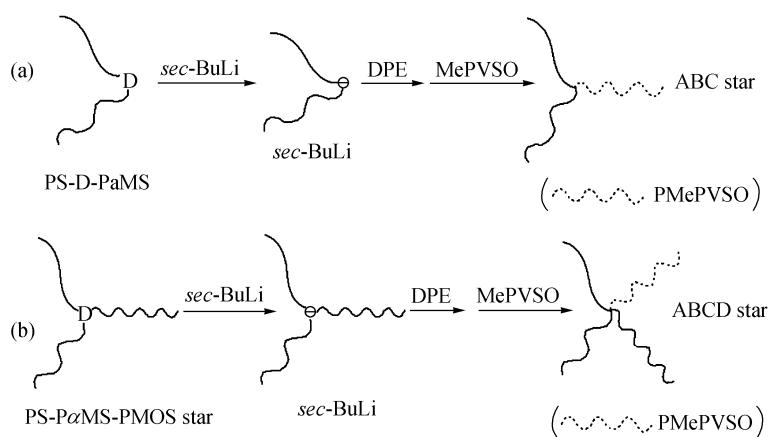
Fig. 2 ¹H-NMR spectra of the isolated AA'B (a), AA'A''B (b) and AA'BC (c–e) stars: (a) S1, (b) S2, (c) S3, (d) S4 and (e) S5

For star polymers, the SEC approach is not the method of choice to determine the real molecular weight due to the difference in hydrodynamic volumes between star polymer and linear polystyrene with same molecular weight. In this study, the molecular weight of various samples was determined by ¹H-NMR and SLS, and the polymerization results are shown in Table 2. In Table 2, the M_n (NMR) value was calculated from the ratios of integrated peak areas of the methyl protons of the initiator fragment ($\delta = 0.5$ – 0.8) and characteristic signals of various segments (Fig. 2). The resonances characteristic to PMOS, P α MS, PTMSS and PMePVSO

segments are $\delta = 3.72$ (methoxy protons), -0.1 – 0.45 (methyl protons), 0.22 (silylmethyl protons) and 2.36 (methyl protons), respectively. On the basis of the chain length of various segments calculated from $^1\text{H-NMR}$, the weight composition of star polymers was obtained. From Table 2, it is found that the molecular weight values of various ABC stars determined by $^1\text{H-NMR}$ and SLS agreed well with those expected, and the weight composition determined by $^1\text{H-NMR}$ analysis was in good agreement with the calculated value. The above results indicate the target star polymers were successfully prepared by the *in situ* initiated anionic polymerization using excessive DPE-functionalized polymers.

Synthesis of 3-Arm ABC and 4-Arm ABCD Heteroarm Star Polymers by Anionic Polymerization Using DPE-Functionalized Polymers in the Presence of Excess *sec*-BuLi

In an alternative methodology, the star polymers are synthesized by the addition reaction of DPE moiety in DPE-functionalized polymers with excess *sec*-BuLi, and followed by the living anionic polymerization of MePVSO initiated from the two types of 1,1-diphenylalkyl anions generated by addition reaction (Scheme 3). All the ABC and ABCD star polymers have one PS segment and one PMePVSO segment, and the other arms are P α MS, PMOS and PTMSS segments, respectively.



Scheme 3 Synthesis of ABC and ABCD heteroarm star polymers by living anionic polymerization using DPE-functionalized polymers in the presence of excess *sec*-BuLi

First, the DPE moiety of the chain-functionalized or core-functionalized polymers was reacted with excess *sec*-BuLi (1.5–2.0 fold excess) to convert to the corresponding polymer anion with two or three different segments. Second, the excess unreacted *sec*-BuLi was capped with DPE to convert to 3-methyl-1,1-diphenylpentyl anion. Last, the living anionic polymerization of MePVSO was subsequently performed in THF at -78°C for 24 h in the presence of a 20-fold or more excess of LiBr. Accordingly, MePVSO underwent the anionic polymerization not only with the 1,1-diphenylalkyl polymer anion *in situ* generated in each macromonomer but also 3-methyl-1,1-diphenylpentyl anion produced by capping the excess *sec*-BuLi, resulting in the formation of the objective star polymer and PMePVSO homopolymer as a byproduct in each case. After reaction, the polymerization was quenched with degassed methanol and the polymer mixture was precipitated by pouring into a large amount of hexane. The polymer mixture was quantitatively obtained in each case. All of the star polymers could be quantitatively isolated from the polymer mixture by selective precipitation into methanol which was a good solvent for PMePVSO.

Figure 3(a, c, e and g) shows SEC profiles of the original reaction mixtures. In SEC profiles of the isolated star polymers, only two peaks corresponding to the objective star and PMePVSO homopolymer formed as a byproduct were noted. As shown in Fig. 3(b, d, f and h), all of the isolated star polymers exhibited symmetric sharp monomodal SEC distributions, with M_w/M_n values being less than 1.03. Meanwhile, the homopolymer PMePVSO could be recovered in quantitative yield in each case by evaporating the methanol solution, followed

by precipitation into hexane. From dashed lines in Fig. 3, it can be seen that the isolated homopolymers almost possess monomodal SEC distributions with M_w/M_n values less than 1.10.

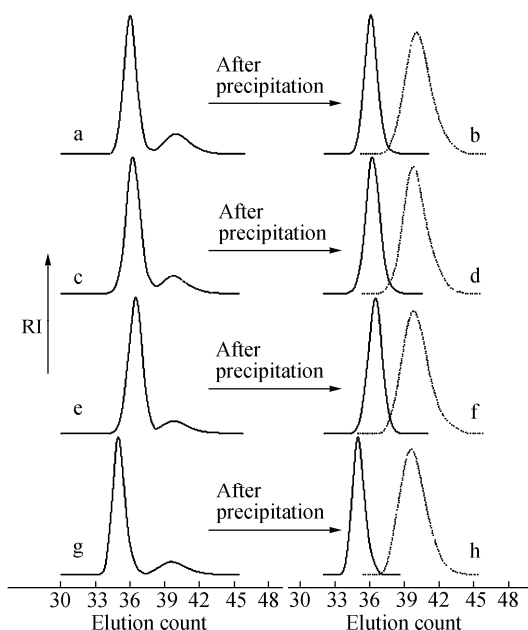


Fig. 3 SEC profiles of the resulting reaction mixtures (a, c, e, g) and isolated star polymers (solid line) and linear PMePVSO homopolymers (dashed line): (b) S6, (d) S7, (f) S8 and (h) S9

During polymerization, the polymer anion and 3-methyl-1,1-diphenylpentyl anion may compete with each other, leading to different chain length of PMePVSO segment in star polymer and linear homopolymer. In this study, it is assumed that both anions possess the same initiating activity for anionic polymerization of MePVSO to afford polymers with same molecular weight, and the theoretical number-average molecular weight ($M_n(\text{calcd})$) and weight composition of the stars were then determined by their feed ratios (Table 3). In Table 3, the absolute weight-average molecular weight (M_w) values were determined by SLS, and the $M_n(\text{NMR})$ values were determined from the ratios of integrated peak areas of the methyl protons of the initiator fragment ($\delta = 0.5\text{--}0.8$) and each of the signals characteristic to PS, PMePVSO, PMS, PMOS and PTMSS. The ^1H -NMR spectra of these star polymers are shown in Fig. 4.

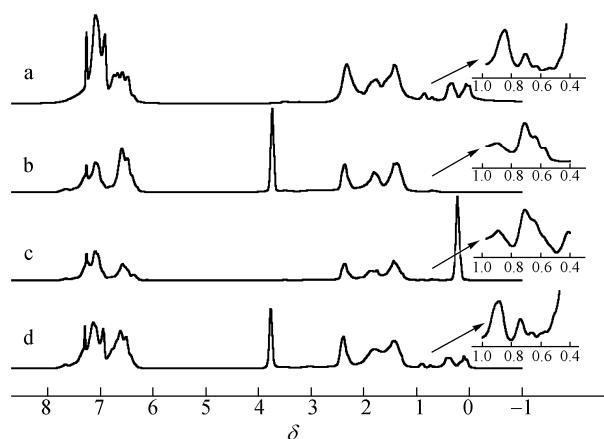


Fig. 4 ^1H -NMR spectra of the isolated ABC (a–c) and ABCD (d) stars: (a) S6, (b) S7, (c) S8 and (d) S9

Table 3. Synthesis of ABC and ABCD star polymers by anionic polymerization of MePVSO initiated from *in situ* formed polymer anion and 3-methyl-1,1-diphenylpentyl anion in THF at -78°C

Sample ^a	M_n			M_w		M_w/M_n^b	Composition	
	Calcd	SEC ^b	¹ H-NMR ^c	Calcd	SLS ^d		Calcd ^e	¹ H-NMR ^f
S6	30200	23600	30500	30800	31500	1.02	32/34/34	31/33/36
S7	30600	22400	31100	31200	32200	1.02	31/34/35	31/33/36
S8	29600	20800	30300	30200	31700	1.02	32/33/35	32/33/35
S9	42200	31200	42700	43000	44200	1.02	23/24/28/25	22/24/28/26

^a S6–S8: ABC stars where A was PS, C was PMePVSO, and B was P α MS (S6), PMOS (S7), and PTMSS (S8); S9: ABCD star where A, B, C and D segments were PS, P α MS, PMOS and PMePVSO, respectively;

^b Estimated by SEC; ^c Determined by ¹H-NMR; ^d Determined by SLS, and the dn/dc values of samples S6 to S9 were 0.174, 0.173, 0.172 and 0.175 mL/g, respectively; ^e Theoretical weight composition of A/B/C (S6–S8) and A/B/C/D (S9) of various stars; ^f Weight composition determined by ¹H-NMR

From Table 3, it is found that the $M_n(\text{calcd})$ values are in good agreement with those of $M_n(\text{NMR})$ in all cases, and the $M_w(\text{calcd})$ values are also similar to the $M_w(\text{SLS})$ ones. The weight compositions determined by ¹H-NMR spectra are very close to the values calculated from feed ratios. Interestingly, the molecular weight of PMePVSO segment introduced into each star was found to be close to that of the recovered homopolymer (Table 4). These results are in good agreement with our previous finding^[20] and further support the above-mentioned assumption that 1,1-diphenylalkyl polymer anion and 3-methyl-1,1-diphenylpentyl anion almost possess the same initiating activity for the anionic polymerization of MePVSO to afford the polymers with similar chain length, which can be ascribed to significantly decreased initiating activity of 1,1-diphenylalkyl anion in the presence of large excess of LiBr additive. Thus, the anionic polymerization of MePVSO initiated from two types of living anions could also afford the expected 3-arm ABC and 4-arm ABCD heteroarm star polymers with one PMePVSO segment.

Table 4. M_n and M_w/M_n values of PMePVSO arm in star polymers and PMePVSO homopolymers recovered from the solution

Original sample	$M_n(\text{in star})^a$	$M_n(\text{recovered})^b$	$M_n(\text{calcd})^c$	$M_n(\text{SEC})^d$	M_w/M_n^d
S6	10900	11200	10400	8330	1.09
S7	11200	11800	10700	8720	1.08
S8	10600	11600	10400	8540	1.10
S9	11100	12000	10600	9060	1.08

^a M_n values of PMePVSO arm introduced into star determined by ¹H-NMR; ^b M_n values of recovered PMePVSO determined by ¹H-NMR; ^c Theoretical values calculated by assuming two types of 1,1-diphenylalkyl anions possess same initiating activity, $M_n(\text{calcd}) = 166 \times [\text{MePVSO}]_0/[\text{sec-BuLi}]_0$; ^d Determined by SEC using polystyrene standards

CONCLUSIONS

A series of heteroarm star polymers containing conductive polyacetylene precursor-PMePVSO were synthesized by two distinct methodologies based on living anionic polymerization using DPE-functionalized polymer. The first methodology involves an addition reaction of living anionic polymer with excess DPE-functionalized polymer and the subsequent anionic polymerization of MePVSO initiated from the *in situ* formed polymer anion with two or three polymer segments, in which the target AA'B, AA'A'B and AA'BC star polymers could be obtained with isolated yield beyond 85%. The second methodology comprises the addition reaction of DPE moiety of DPE-functionalized polymers with excess *sec*-BuLi and the following living anionic polymerization of MePVSO initiated from the two types of 1,1-diphenylalkyl anions generated by addition reaction, in which the objective ABC and ABCD star polymers were achieved in nearly quantitative yield after selective precipitation into methanol. The isolated star polymers possess predetermined molecular weight, narrow molecular weight distribution ($M_w/M_n < 1.03$) and desired composition, as confirmed by SEC, ¹H-NMR and SLS.

ACKNOWLEDGMENT The authors appreciate Prof. Akira Hirao at Tokyo Institute of Technology, Japan for his continuous support and direction to this study.

REFERENCES

- 1 Matyjaszewski, K. and Xia, J., *Chem. Rev.*, 2001, 101: 2921
- 2 Hawker, C.J., Bosman, A.W. and Harth, E., *Chem. Rev.*, 2001, 101: 3661
- 3 Kamigaito, M., Ando, T. and Sawamoto, M., *Chem. Rev.*, 2001, 101: 3689
- 4 Hadjichristidis, N., Pitsikalis, M., Pispas, S. and Iatrou, H., *Chem. Rev.*, 2001, 101: 3747
- 5 Hirao, A., Hayashi, M., Loykulnant, S., Sugiyama, K., Ryu, S.W., Haraguchi, N., Matsuo, A. and Higashihara, T., *Prog. Polym. Sci.*, 2005, 30: 111
- 6 Fujimoto, T., Zhang, H., Kazama, T., Isono, Y., Hasegawa, T. and Hashimoto, T., *Polymer*, 1992, 33: 2208
- 7 Li, Z.B., Kesselman, E., Talmon, Y., Hillmyer, M.A. and Lodge, T.P., *Science*, 2004, 306: 98
- 8 He, X.H., Huang, L., Liang, H.J. and Pan, C.Y., *J. Chem. Phys.*, 2003, 118: 9861
- 9 Tang, P., Qiu, F., Zhang, H.D. and Yang, Y.L., *J. Phys. Chem. B*, 2004, 108: 8434
- 10 Feng, X.S. and Pan, C.Y., *Macromolecules*, 2002, 35: 2084
- 11 Feng, X.S. and Pan, C.Y., *Macromolecules*, 2002, 35: 4888
- 12 Deng, G.H., Zhang, L.W., Liu, C.D., He, L.H. and Chen, Y.M., *Eur. Polym. J.*, 2005, 41: 1177
- 13 Luo, Z.H., Fu, Z.F. and Shi, Y., *Chinese J. Polym. Sci.*, 2008, 26(3): 321
- 14 Dong, Y.Q., Dong, B.T., Du, F.S., Meng, J.Q. and Li, Z.C., *Polymer*, 2009, 50: 125
- 15 Wei, J. and Huang, J.L., *Macromolecules*, 2005, 38: 1107
- 16 Zhang, Y.F., Li, C.H. and Liu, S.Y., *J. Polym. Sci. Part A: Polym. Chem.*, 2009, 47: 3066
- 17 Higashihara, T. and Hirao, A., *J. Polym. Sci. Part A: Polym. Chem.*, 2004, 42: 4535
- 18 Higashihara, T., Nagura, M., Inoue, K., Haraguchi, N. and Hirao, A., *Macromolecules*, 2005, 38: 4577
- 19 Zhao, Y.L., Higashihara, T., Sugiyama, K. and Hirao, A., *J. Am. Chem. Soc.*, 2005, 127: 14158
- 20 Zhao, Y.L., Higashihara, T., Sugiyama, K. and Hirao, A., *Macromolecules*, 2007, 40: 228
- 21 Hirao, A., Higashihara, T. and Inoue, K., *Macromolecules*, 2008, 41: 3579
- 22 Higashihara, T., Sakurai, T. and Hirao, A., *Macromolecules*, 2009, 42: 6006
- 23 Altintas, G., Hizal, G. and Tunca, U., *J. Polym. Sci. Part A: Polym. Chem.*, 2008, 46: 1218
- 24 Yang, L.P., Zhou, H., Shi, G., Wang, Y. and Pan, C.Y., *J. Polym. Sci. Part A: Polym. Chem.*, 2008, 46: 6641
- 25 Wang, G.W., Lou, X.L. and Huang, J.L., *J. Polym. Sci. Part A: Polym. Chem.*, 2008, 46: 2154
- 26 Wang, X., He, J. and Yang, Y., *J. Polym. Sci. Part A: Polym. Chem.*, 2007, 45: 4818
- 27 Kanga, R.S., Hogen-Esch, T.E., Randrianalimanana, E., Soum, A. and Fontanille, M., *Macromolecules*, 1990, 23: 4235
- 28 Reibel, D., Nuffer, R. and Mathis, C., *Macromolecules*, 1992, 25: 7090
- 29 Leung, L.M. and He, W.D., *Synth. Metals*, 2001, 122: 263
- 30 Bader, A. and Wünsch, J.R., *Macromolecules* 1995, 28: 3794
- 31 Leung, L.M. and Tan, K.H., *Polymer*, 1994, 35: 1556
- 32 Wu, C., Niu, A., Leung, L.M. and Lam, T.S., *J. Am. Chem. Soc.*, 1999, 121: 1954
- 33 Leclère, Ph., Hennebicq, E., Calderone, A., Brocorens, P., Grimsdale, A.C., Müllen, K., Brédas, J.L. and Lazzaroni, R., *Prog. Polym. Sci.*, 2003, 28: 55
- 34 Hoebe, F.J.M., Jonkheijm, P., Meijer, E.W. and Schenning, A.P.H., *J. Chem. Rev.*, 2005, 105: 1491
- 35 Ishizone, T., Sugiyama, K., Hirao, A. and Nakahama, S., *Macromolecules*, 1993, 26: 3009