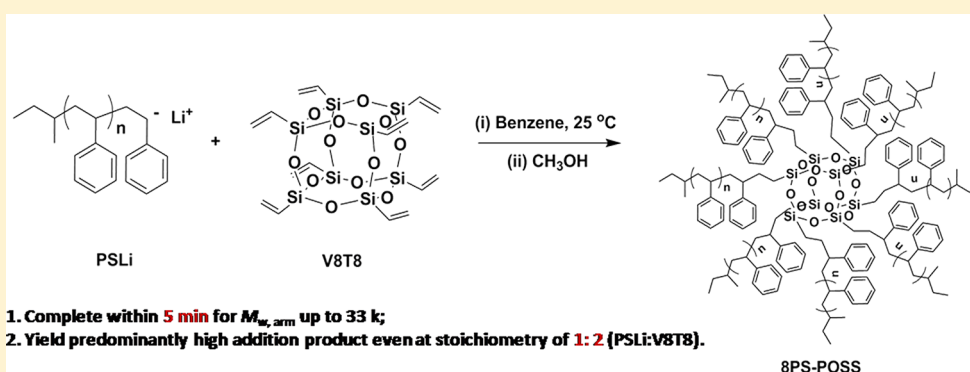


Rapid and Efficient Anionic Synthesis of Well-Defined Eight-Arm Star Polymers Using OctavinylPOSS and Poly(styryl)lithium

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S Supporting Information



ABSTRACT: A new approach has been developed for the preparation of well-defined, eight-arm star polymers via the addition of poly(styryl)lithium to octavinylPOSS in benzene. The reaction proceeds rapidly to completion (within 5 min for molecular weight of each arm up to 33 kg/mol), forming predominantly eight-arm star polymers. The products were purified by fractionation and fully characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, FT-IR, MALDI-TOF mass spectrometry, and size exclusion chromatography. Compared to conventional coupling approaches, this process is found to be less sensitive to the stoichiometry of the reactants and the molecular weight of each arm. A mechanism based on cross-association and intra-aggregate addition is invoked to account for this unusual observation. As evidence, when a polar solvent, tetrahydrofuran, or a strongly coordinating and disassociating Lewis base, tetramethylethylenediamine, was used to dissociate the living polymer chains, star polymers with lower average arm numbers than those of the products synthesized in pure benzene were formed at the same stoichiometry of the reactants. The method has general implications in the understanding of the reactive nature of the living anionic polymerization and may find practical application in the synthesis of functional star polymers of diverse compositions and architectures.

INTRODUCTION

Star polymers are branched polymers characterized by multiple linear chains linked to a central core.^{1–9} The unique topology imparts valuable properties that are depending critically on the molecular parameters such as number of arms, molecular weight of each arm, chemical composition, and polydispersity. The precise and convenient synthesis of such star polymers has been a subject of intense study even since the early days of polymer science. With the advent of living anionic polymerization¹ and other controlled polymerization techniques,^{10,11} many methods have been developed toward this end by using multifunctional initiators, multifunctional linking agents, or difunctional monomers, following either an “arm-first”^{12–17} or “core-first” strategy.^{18–22} Furthermore, star polymers with asymmetric composition, heteroarm identity, and complex architecture (e.g., star-block copolymers, miktoarm, and

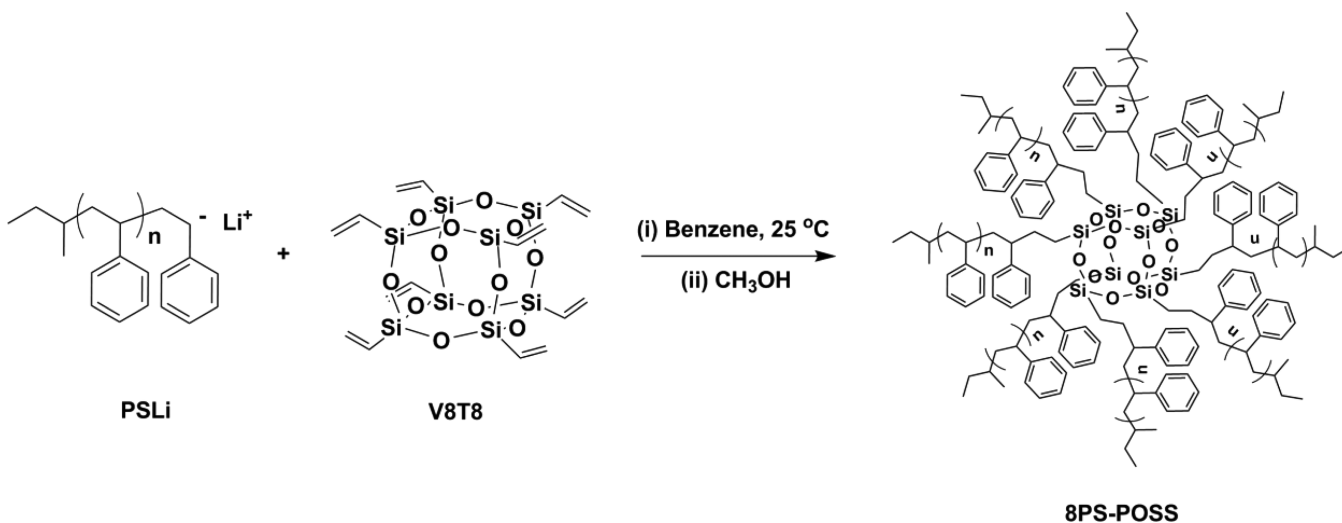
asymmetric star polymers) have also been prepared.^{3,6–9,23} Although sufficient levels of control have been demonstrated, the methods often suffer either from prolonged reaction time and incomplete reaction due to the steric hindrance of the coupling reaction in the “arm-first” strategy or from the unequal initiation efficiency and poor control over polymer chain uniformity in the “core-first” strategy.¹ In the case of using difunctional monomers, the overall molecular structure and the number of arms are often not well-defined, polydispersity is often relatively large, and an average arm number is often given.^{24,25} While these methods can suffice for most applications, fundamental study requires star polymers with

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Scheme 1. Addition of PSLi to V8T8 Yields Predominantly Eight-Arm Star Polymer (8PS-POSS)



well-defined structures and low degree of compositional heterogeneity with respect to molecular weight and molecular weight distribution. So far, it remains a challenge to prepare uniform star polymers with molecular precision in a rapid and efficient process.

Living anionic polymerization of styrenic and dienic monomers initiated by organolithium compounds provides a useful and reliable method for the construction of polymers with complex structures and perhaps the lowest degree of constitutional heterogeneity.^{1,5,26} The reactive nature of the living carbanionic chain-end allows the use of various linking agents, such as silyl halides and 1,1-diphenylethylene derivatives, for deliberate controlled termination/coupling reactions and/or a second polymer chain growth.⁹ However, the process depends critically on the relative stoichiometry between the arm and the linking agent (where a large excess of arm is commonly practiced), the chain-end structure (where steric hindrance plays a significant role), the chemistry of the coupling reaction (which should proceed without side reactions even over prolonged reaction times), and the molecular weight of each arm (which affects the reactivity of the chain end and the efficiency of the coupling reaction).^{12,27}

Polyhedral oligomeric silsesquioxane (POSS) is a family of nanosized cage-like compounds with rigid three-dimensional structure, well-defined molecular shape, and versatile surface chemistry.^{28–31} Because of the presence of multiple functional groups, it has been used as the core for dendrimers as well as hyperbranched and star polymers.^{28,31,32} For example, star polystyrene and poly(methyl methacrylate) could be grown from POSS-based multi-initiators POSS-(Br)₈ using atom-transfer radical polymerization (ATRP) and RAFT polymerization.^{33,34} Kim et al.³⁵ reported the hydrosilylation reaction between silyl hydride-functionalized polystyrene (PS) and octavinylPOSS to prepare eight-arm star polymer. Both “grafting-to” and “grafting-from” approaches have been demonstrated by Kuo et al. and Hwang et al. in the synthesis of various POSS-based star polymers, including poly(γ -benzyl-L-glutamate) and poly(methyl methacrylate).^{36,37} It is noteworthy that Bening³⁸ reported the reaction of living anionic chain with octa-substituted POSS in hydrocarbons at elevated temperatures as a way to prepare radial polymers in a recent patent disclosure. The star polymer formation in this case was achieved under rather drastic conditions where the POSS cage

was opened to form the core. There is yet no detailed account on the precise structure of the product and the mechanism of such a reaction.

In this paper, we report a method for the preparation of precisely defined eight-arm star polymers based on the reaction of poly(styryl)lithium and octavinylPOSS. The process was found to be less sensitive to stoichiometry and arm molecular weights in the presence of nonpolar solvents and can reach completion generally within 5 min. The unusual independency on stoichiometry and arm molecular weight was tentatively explained by a cross-association-promoted intra-aggregate addition mechanism.

EXPERIMENTAL SECTION

Chemicals and Solvents. Benzene (Certified ACS, EM Science), tetrahydrofuran (THF, Certified ACS, EM Science), and styrene (99%, Aldrich) were purified as previously reported.³⁹ Benzene and THF were distilled as needed from PSLi into the polymerization reactors. *sec*-Butyllithium (12 wt % in cyclohexane, FMC Lithium) was used as received after double titration with allyl bromide.⁴⁰ *N,N,N',N'*-Tetramethylethylenediamine (TMEDA, Aldrich, 99%) was stirred over calcium hydride and freeze-degassed several times on the vacuum line before distillation into calibrated ampules that were flame-sealed off the line. OctavinylPOSS (V8T8, >97%, Hybrid Plastics) was dried in high vacuum at 90 °C for 4 h immediately before use. Methanol (Reagent grade, Fisher Scientific) was degassed on the vacuum line and distilled into ampules that were subsequently flame-sealed off the line.

Characterization. Size exclusion chromatographic (SEC) analyses for the synthesized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10³/10⁴ Å), mixed bed (10³, 10⁴, 10⁶ Å)], and a triple detector system. The three detectors included a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, λ = 670 nm). THF was used as the eluent with a flow rate of 1.0 mL/min at 35 °C. The literature refractive index increment (dn/dc) value of 0.185 mL/g was used for linear polystyrene-based samples. For star polystyrenes, the dn/dc value was determined using the BI-DNDC differential refractometer from the Brookhaven Instruments Corp. Prior to measurements, the instrument was calibrated with a series of KCl aqueous solutions with different concentrations under identical conditions. The dn/dc value of the star PS in THF solution at 35 °C was measured to be 0.197 mL/g, which is close to literature results^{41–43} and used for all of the star polymer molecular weight calculations in this paper.

All ^1H , ^{13}C , and ^{29}Si NMR spectra were acquired in CDCl_3 (Aldrich, 99.8% D) using a Varian 500 MHz NMR spectrometer. The ^1H NMR spectra were referenced to the residual proton impurities in CDCl_3 at δ 7.27 ppm. The ^{13}C NMR spectra were referenced to $^{13}\text{CDCl}_3$ at δ 77.00 ppm. The ^{29}Si NMR spectra were referenced to tetramethylsilane in the CDCl_3 at δ 0 ppm.

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA) by casting polymer films on KBr plates from solution with subsequent drying at 40–50 °C. The data were processed using Win-IR software.

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All spectra were measured in positive reflection or linear mode. The instrument was calibrated prior to each measurement with external PMMA or PS standards at the molecular weight under consideration. *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, >99%) served as matrix and was prepared in CHCl_3 at a concentration of 20 mg/mL. Silver trifluoroacetate (AgTFA) served as cationizing agent and was prepared in $\text{MeOH}/\text{CHCl}_3$ (*v/v* = 1/3) as a 10 mg/mL solution. Polystyrenes were dissolved in CHCl_3 at a concentration of 5 mg/mL. The matrix and AgTFA were mixed with the ratio of 10/1 (*v/v*). The sample preparation involved depositing 0.5 μL of matrix and salt mixture on the wells of a 384-well ground-steel plate, allowing the spots to dry, depositing 0.5 μL of each sample on a spot of dry matrix, and adding another 0.5 μL of matrix and salt mixture on top of the dry sample. After evaporation of the solvent, the plate was inserted into the MALDI source. The attenuation of the Nd:YAG laser was adjusted to minimize unwanted polymer fragmentation and to maximize the sensitivity. The mass scale was calibrated externally using the peaks obtained from a PS or PMMA standard at the molecular weight range under consideration. Data analyses were conducted with Bruker's flexAnalysis software.

General Procedure for the Polymerization and Coupling Reaction with OctavinylPOSS (V8T8). Living PSLi was prepared under high-vacuum conditions in sealed, all-glass reactors using *sec*-butyllithium as the initiator in benzene at 30 °C (10–15 vol % monomer).³⁹ PSLi solution was then distributed to several ampules which were then sealed off the reactor. The remaining solution in the reactor was quenched with methanol to give the base PS. For reactions in THF, benzene was removed by freeze-drying and THF was distilled in to make a solution which was kept at –78 °C before reaction. Since PSLi is known to decompose over long time in THF at room temperature,⁴⁴ the solution was only allowed to warm up to 0 °C immediately before reaction and the reaction time was limited to 30 min. For the reaction with TMEDA additives, the PSLi ampule was made with a side-attached TMEDA ampule. The PSLi ampule was connected to another glass reactor by glass blowing techniques. After attaching the whole reactor to the high-vacuum line, the V8T8 was weighed into the reactor under argon and dried in high vacuum at 90 °C for 4 h before benzene or THF was transferred into the reactor. The whole reactor was then flame-sealed off the high vacuum line. After the solvent completely thawed, the PSLi solution was added to the solution of V8T8 by smashing the break-seal of the PSLi ampule at 25 °C. For the reaction with TMEDA additives, the break-seal of the TMEDA ampule was first smashed to mix TMEDA and PSLi for a period of 3 min before its subsequent addition into the V8T8 solution. Aliquots of the reaction mixture were taken by flame-sealing off an ampule at designated time intervals (e.g., 5 min, 2 h, and 36 h). The reaction mixture was quenched with methanol followed by precipitation into cold methanol. The white solid was collected as the crude product and was further purified by fractional precipitation using toluene/methanol as the solvent/nonsolvent pair.

Eight-Arm Polystyrene (8PS-POSS). A poly(styryl)lithium (M_n = 1.2 kg/mol, PDI = 1.06) was reacted with V8T8 in a ratio of 8.3:1 in benzene at 25 °C. After fractional precipitation in toluene/methanol, pure eight-arm star polymer was obtained as a white powder (8PS-POSS). Yield: 30–40%. ^1H NMR (CDCl_3 , 500 MHz, ppm, δ): 7.50–6.25 (m, 385H), 2.55–0.85 (m, 272H), 0.80–0.60 (m, 48H, $-\text{CH}_3$).

^{13}C NMR (CDCl_3 , 125 MHz, ppm, δ): 145.9, 128, 127.6, 125.6, 46.5–43, 40.5, 31.5, 30.5–28.2, 20.0–18.2, 11.3–10.6. FT-IR (KBr) ν (cm^{-1}): 3026, 2922, 1945, 1868, 1808, 1743, 1601, 1492, 1448, 1111 (Si–O–Si asymmetric stretching), 760, 689. MS (MALDI-TOF, *m/z*): Calcd average mass for 80-mer with a silver ion ($[\text{M}_{80}\cdot\text{Ag}]^+$, $\text{C}_{688}\text{H}_{744}\text{AgO}_{12}\text{Si}_8$): 9537.8 Da. Found: 9537.6 Da. SEC: $M_{n,\text{SEC}}$ = 10.5 kg/mol, $M_{w,\text{SEC}}$ = 11.0 kg/mol, PDI = 1.05.

RESULTS AND DISCUSSION

Preparation of 8PS-POSS. The unique feature of “living” polymeric anions such as PSLi is their ability to undergo further chain growth, block polymerization, or controlled termination to give rise to polymers of complex architecture.^{1,45} The highly reactive organolithium chain end can react with a large variety of functional groups, such as vinyl, epoxy, silyl halide, alkyl halide, and carbonyl compounds.¹ In the case of vinylsiloxanes (such as V8T8 in this case), the presence of a silicon atom adjacent to the vinyl group promotes the electrophilicity of the vinyl group by partial overlapping of the d-orbital of silicon atom with the double bond, making it susceptible to nucleophilic addition (such as that from PSLi).^{46,47} However, to use V8T8 as a well-defined core for star polymer synthesis under anionic conditions, we must first examine if it is possible for PSLi to directly react with POSS in benzene to open the cage. Control experiments were performed by reacting excess PSLi (8.3 equiv) with octaisobutylPOSS (1 equiv) in benzene at room temperature. The red color of the living anions persisted even after 12 h. After quenching with methanol, the products were collected and analyzed by SEC (Figure S1). All of them showed up as monomodal peaks at essentially identical retention volume as the base PS, which suggests that there is no reaction occurring between PSLi and octaisobutylPOSS cage in benzene at room temperature. In other words, the reaction, if any, shall occur exclusively by addition of PSLi across vinyl groups on POSS.

The synthesis was then performed by reacting 8.3 equiv of PSLi to 1 equiv of V8T8. For ease of characterization, a PSLi of relatively low molecular weight (M_n = 1.2 kg/mol, PDI = 1.06) was utilized. The PSLi solution was directly added into the solution of V8T8 in benzene in one portion. The reverse addition was found to give identical results (data not shown). Upon the addition of PSLi, the red color disappeared rapidly within 1 min, and the solution turned light yellow. The reaction mixture was quenched after 2 h. To explicitly characterize the structure, the product was further purified by fractional precipitation to remove low molecular weight impurities with favorable mass recovery (30–40%). The SEC overlay of the base polymer, crude product, and fractionated product is shown in Figure 1. The trace of the crude product shows a huge shift to smaller retention volume compared with that of the base PS, and the molecular weight is close to 8 times that of the base polymer (Table 1). The fractionated sample has a narrow polydispersity (PDI = 1.05) and a molecular weight (M_n = 10.5 kg/mol) similar to the expected value for an eight-arm star product ($M_{n(\text{calcd})}$ = 10.2 kg/mol). The average arm number based on M_w also equals 8.0.

The well-defined structure of the fractionated eight-arm star polymer was further characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, and MALDI-TOF mass spectrometry. As seen in the ^1H NMR spectra in Figure 2, the complete disappearance of the peaks around δ 5.90–6.18 ppm is unambiguous evidence that the reaction takes place by nucleophilic addition of PSLi to vinyl groups. This is also supported by the ^{13}C NMR spectra

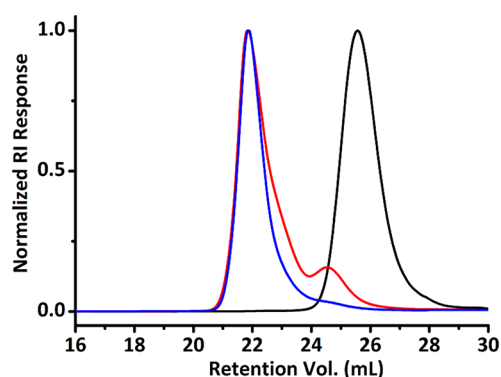


Figure 1. SEC overlay of the base PS ($M_n = 1.2$ kg/mol, PDI = 1.06, black), the crude product obtained after 2 h of addition reaction (red), and the fractionated eight-arm star PS, 8PS-POSS ($M_n = 10.5$ kg/mol, PDI = 1.05, blue). The reaction was carried out at a ratio of 8.3:1 (PSLi:V8T8) in benzene.

shown in Figure S2 where the vinyl peaks of V8T8 cannot be observed in the product. Furthermore, the fact that the POSS cage structure remains intact after reaction is supported by the single peak at $\delta -67.0$ ppm in the ^{29}Si NMR spectrum shown in Figure 3. Compared to that of V8T8 at $\delta -74.9$ ppm, it shows a relatively downfield shift that is consistent with literature report.⁴⁸ In the FT-IR spectrum (Figure S3), the symmetric bending/stretching of the Si–O–Si bond from POSS cage can still be observed at around 1111 cm^{-1} , which is another evidence for the presence of the POSS cage as the core in the final product.

The most striking structural evidence comes from the MALDI-TOF mass spectrometry. As shown in Figure S4, the base PS gives a single molecular weight distribution, and the observed molecular weight is in excellent agreement with the calculated one. Despite the relatively high molecular weight of 8PS-POSS, a clean MALDI-TOF mass spectrum (see Figure 4) was still obtained where only one single distribution could be observed. Although monoisotopic resolution is not possible in this molecular weight range, the average molecular weights of the peaks match well with the calculated value (e.g., for $[\text{M}_{80}\text{Ag}]^+$ with the formula of $\text{C}_{688}\text{H}_{744}\text{AgO}_{12}\text{Si}_8$, obsd m/z 9537.6 Da vs calcd 9537.8 Da). The data also attest to the homogeneity of the sample. The average molecular weights obtained from MALDI-TOF are lower than those obtained from SEC, apparently due to reduced ionizability of higher molecular weight fractions and the preferential ionization of lower molecular weight fractions.⁴⁹ Nevertheless, the above evidence has unambiguously established the chemical structure and purity of the star polymer, 8PS-POSS.

Effect of Reaction Time, Molecular Weight, and Stoichiometry. To evaluate the effect of different reaction conditions on the final product formation, a series of experiments were performed. The stoichiometry was first fixed at a ratio of PSLi:V8T8 = 8.3:1 to study the effect of reaction time and arm molecular weights. It is known that the extent and efficiencies of the coupling reactions in the traditional polychlorosilane approach to star polymers are dependent upon the steric requirements of the carbanionic chain end, which is in turn related to both the chemical structure of the chain end and the molecular weight of each arm.^{12,27} Therefore, it is intriguing to look into the effect of arm molecular weight on coupling efficiency. PSLi samples of several molecular weights up to 237 kg/mol were reacted with

Table 1. Summary of the Molecular Characterizations of Different Samples Reported

sample	$M_{n,\text{SEC}}$ (kg/mol) ^a	$M_{w,\text{SEC}}$ (kg/mol) ^a	PDI ^a	n^b	note ^c
base PS	1.2	1.3	1.06		Figure 1
2 h crude	9.0	9.6		6.9	Figure 1
fractionated	10.5	11.0	1.05	8.0	Figure 1
base PS	6.7	6.9	1.03		Figure Sa
5 min crude	46.8	48.8		7.0	Figure Sa
2 h crude	45.6	48.9		7.0	Figure Sa
fractionated	56.7	58.9	1.04	8.4	Figure Sa
base PS	10.5	10.6	1.01		Figure Sb
5 min crude	77.2	79.5		7.4	Figure Sb
2 h crude	80.6	83.8		7.8	Figure Sb
fractionated	84.4	87.8	1.04	8.2	Figure Sb
base PS	33.1	33.4	1.01		Figure Sc
5 min crude	234	239		7.1	Figure Sc
2 h crude	240	245		7.3	Figure Sc
fractionated	251	256	1.02	7.7	Figure Sc
base PS	237	239	1.01		Figure Sd
5 min crude	1291	1343		5.6	Figure Sd
2 h crude	1481	1525		6.4	Figure Sd
36 h crude	1447	1476		6.2	Figure Sd
fractionated	1556	1587	1.02	6.6	Figure Sd
base PS	1.4	1.5	1.06		Figure 6
8.3:1	11.3	12.3		7.8	Figure 6
1:1	8.4	9.3		5.8	Figure 6
1:2	7.4	8.1		5.0	Figure 6
base PS	4.4	4.5	1.02		Figure 7a
in benzene	25.1	27.6		6.0	Figure 7a
in benzene–THF	22.8	25.2		5.5	Figure 7a
in THF	16.3	19.1		4.1	Figure 7a
base PS	4.3	4.4	1.01		Figure 7b
0 equiv TMEDA	21.1	24.3		5.4	Figure 7b
4 equiv TMEDA	8.0	10.3		2.2	Figure 7b
70 equiv TMEDA	5.4	6.0		1.2	Figure 7b

^aFor crude samples, the molecular weights are based on the high-MW peak only, and therefore PDI values of these samples are not calculated. ^bThe average number of arms, n , is calculated based on the equation $n = (M_{w,\text{star}} - M_{w,\text{V8T8}})/M_{w,\text{base}}$. ^cDetailed reaction conditions to afford each sample are described in the notes of the corresponding figures.

V8T8 in benzene. In all cases, the reaction proceeded rapidly and the red color of the PSLi quickly faded and became light yellow within minutes upon addition. Aliquots of the reaction mixture were taken at designated time intervals, quenched, precipitated, and collected for SEC analysis.

The results are shown in Figure 5, and the molecular characterizations are summarized in Table 1. It is clear that the reaction is essentially complete within 5 min for relatively low arm molecular weights up to 33 kg/mol. For these samples, the samples obtained in 5 min and in 2 h are essentially identical, though very slightly increased molecular weights of the 2 h samples were indeed observed. The fractionated samples possess average arm number very close to 8. For even higher arm molecular weights such as 237 kg/mol, the product from 2 h addition reaction shows considerably higher molecular weight than that from 5 min reaction but is almost identical to that from 36 h reaction. The average arm number of the

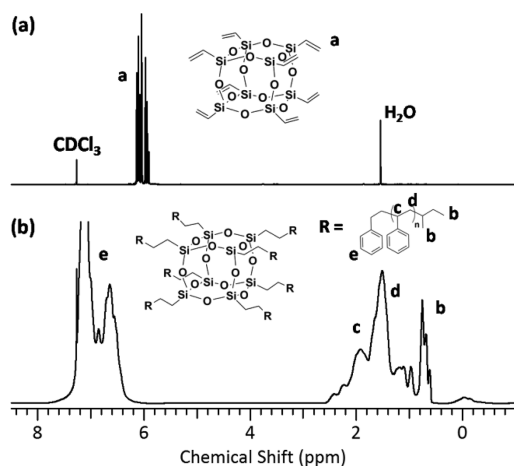


Figure 2. ¹H NMR spectra of (a) V8T8 and (b) the eight-arm star PS (8PS-POSS).

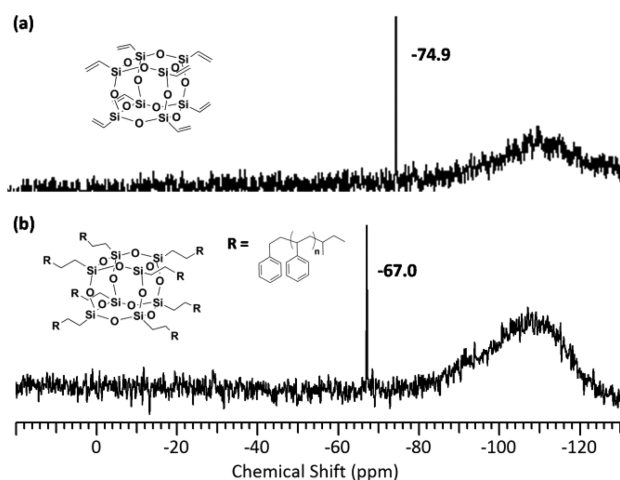


Figure 3. ²⁹Si NMR spectra of (a) V8T8 and (b) the eight-arm star PS (8PS-POSS).

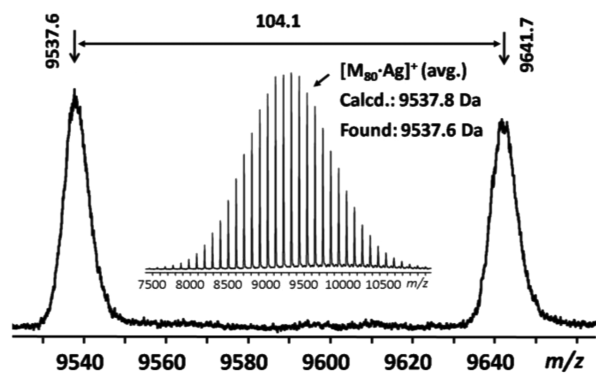


Figure 4. MALDI-TOF mass spectrum of the eight-arm star PS (8PS-POSS) shows one single distribution corresponding to the desired structure. The inset is the overall spectrum.

fractionated sample is only around 6.6, indicating that significant steric hindrance is present for arms of high molecular weights, preventing the reaction from completion. Yet, this is still remarkable since the only a slight excess of PSLi is used. Hence, this is an extremely fast and efficient reaction. Extending reaction time does help drive the reaction more to completion, but not by a lot. Using a large excess of PSLi with higher

molecular weights also did not improve the results (data not shown). Provided enough PSLi, the coupling efficiency seems to be limited mostly by steric hindrance. Considering the highly reactive nature of this reaction between PSLi and VPOSS, these results might represent the limit of arm numbers possible for a specific arm molecular weight in the current approach. This is remarkable comparing to the polychlorosilane coupling approach where a large excess of PSLi ($\text{PLi/Si-Cl} = 1.2\text{--}1.8$) and elevated temperature ($50\text{--}110\text{ }^{\circ}\text{C}$) for extended reaction times (from several days to weeks) are usually required.^{1,12}

Traditionally, it is known that the extents and efficiencies of most linking reactions are dependent upon the steric requirements of the carbanionic chain end in the order of poly(butadienyl)lithium (PBLi) > poly(isoprenyl)lithium (PILi) > PSLi. The least sterically hindered PBLi is thus the most reactive one.⁵⁰ Thus, two common strategies to improve the coupling efficiency are (1) by adding a few units of butadiene to the chain end and (2) by using a more spatially separated coupling agents.⁵⁰ While the less crowded spatial arrangement of vinyl groups on POSS may contribute, in part, to the high coupling efficiency, it is noteworthy that current method works well without butadiene end-capping. It is expected that other carbanionic polymer chain ends (such as PILi and PBLi) should work as well as PSLi, if not better.

So far, the preparation of star polymers by coupling approach usually requires a large excess of the polymer arm (e.g., $1.2\text{--}1.8$ equiv per functional group).¹² Adding less than stoichiometry will usually results in a mixture of star polymers with a statistical distribution of arm numbers, among which the dominant species is predominantly determined by the ratio of the reactants. Hence, by reacting 1 equiv of PSLi with 1 equiv of V8T8, we anticipated that that major product should be mono-VPOSS-end-capped PS (VPOSS-PS), a precursor to recently reported "giant surfactants".^{51,52} However, it was surprisingly found that no matter what the ratios between PSLi and V8T8 are (8.3:1, 1:1, and 1:2), high molecular weight star polymers were always obtained even when V8T8 was present in excess (Figure 6 and Table 1). The result is somewhat counter-intuitive. It was at first speculated that octavinylPOSS might only be partially soluble in benzene at $25\text{ }^{\circ}\text{C}$, and the addition of the first PSLi arm to the octavinylPOSS increases the solubility and thus favors additional arms to be successively attached. However, the solubility of V8T8 in benzene was determined to be larger than 30 mg/mL at $25\text{ }^{\circ}\text{C}$, which is already much higher than the working concentration ($0.03\text{--}6\text{ mg/mL}$). Moreover, before the addition of PSLi, the system was also carefully examined to make sure that all V8T8 had completely dissolved and a homogeneous solution was obtained. Therefore, the results exclude the possibility of V8T8 solubility as a possible explanation. But then what could account for this unusual dependence of product distribution on stoichiometry?

Mechanism of Star Polymer Formation. If we compare the traditional polychlorosilane coupling method for star polymer synthesis and the addition reaction between PSLi and V8T8 in this work, the only difference is that the former leads to a neutral product and lithium chloride salt while the latter gives a charged alkylolithium adduct (RLi) (Figure S5). This unique feature shall be responsible for the unusual lack of dependency of product distribution on stoichiometry in this reaction. A mechanism was thus proposed based on the cross-association between active organometallic species that would

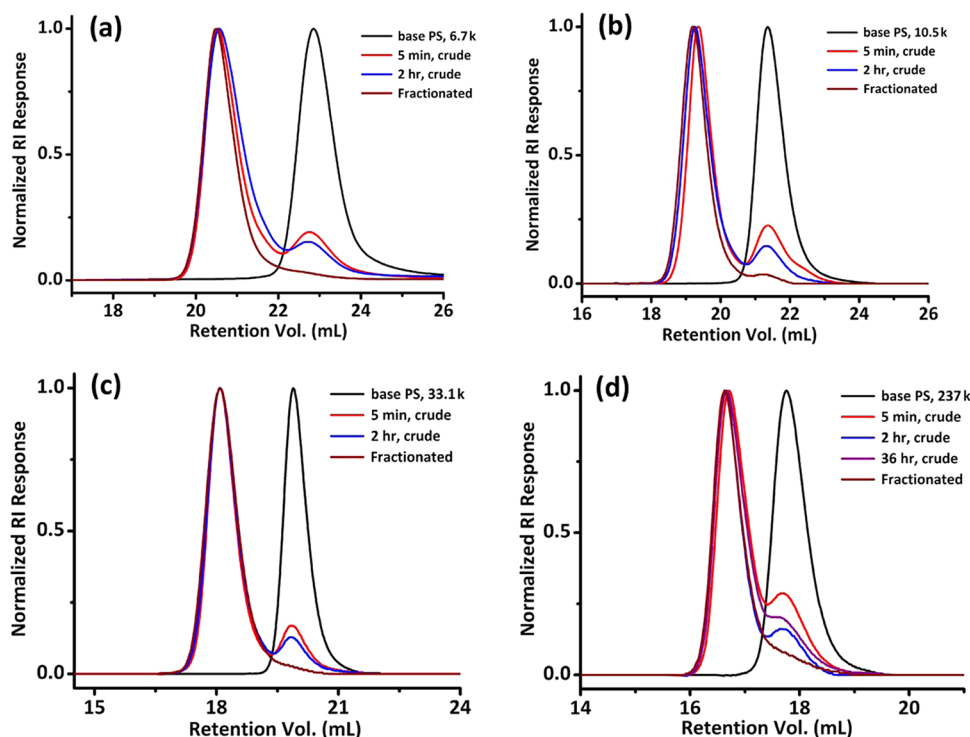


Figure 5. SEC overlay of the base PS (black), the crude products obtained after 5 min (red), 2 h (blue), and 36 h (purple) reaction time, and the fractionated star PS (wine). The base PS has a number-average molecular weight (M_n) of (a) 6.7, (b) 10.5, (c) 33.1, and (d) 237 kg/mol. The reaction was carried out via the addition of PSLi in benzene to a solution of V8T8 in benzene at a ratio of 8.3:1 (PSLi:V8T8).

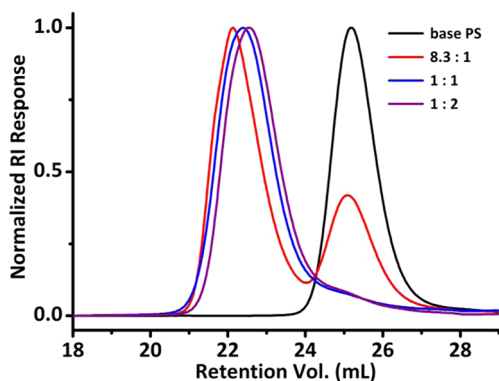


Figure 6. SEC overlay of the base PS ($M_n = 1.4$ kg/mol, PDI = 1.06, black) and the crude product obtained after 30 min addition reaction using 8.3:1 (red), 1:1 (blue), and 1:2 (purple) stoichiometry of PSLi:V8T8. The reaction takes place via the addition of PSLi in benzene to a solution of V8T8 in benzene.

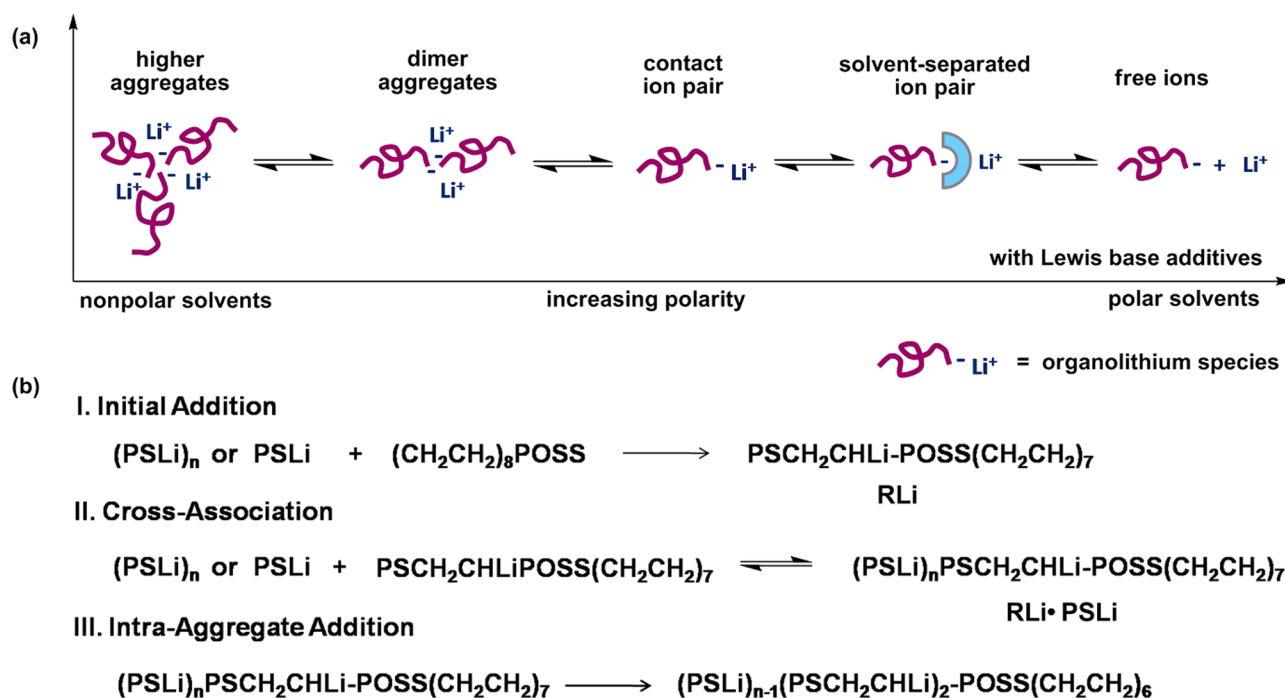
make the vinyl groups on POSS of the intermediates more susceptible toward further addition than those on the intact V8T8 (Scheme 2).

In solution, the active organometallic species exist in a series of equilibria between different forms of aggregates according to the general Winstein spectrum of active species (Scheme 2).^{53,54} For example, poly(styryl)lithium is known to exist predominantly as dimers in hydrocarbon solvent in addition to small amounts of other higher aggregates.⁵⁵ Similarly, the intermediate alkylolithium adduct is also expected to form aggregates in hydrocarbon solvent. Actually, it is known that alkylolithium is much more associated than that of PSLi, typically with degrees of aggregation ranging from 4 to 6.^{56,57} Hence, it is very likely that not only do they associate with other RLi, but

also they cross-associate with unreacted PSLi in solution. To the extent that cross-associated species (RLi·PSLi) are formed, it is expected that the reactive chain ends and vinyl groups are brought into vicinity within the same aggregate, notably promoting the intra-aggregate addition of PSLi to the remaining vinyl groups. Moreover, the higher adducts bear more charges per molecule and possess a much higher charge density. As a result, they are far more prone to cross-association in the presence of nonpolar solvents than monoadducts or diadducts. Therefore, the reaction has a strong tendency to go to completion once initiated and the predominant product is theoretically the eight-arm star PS, irrespective of the stoichiometry between PSLi and V8T8. This feature is very similar to the electrostatic self-assembly and covalent fixation method for cyclic polymer synthesis reported by Tezuka et al.⁵⁸ and the DNA templated organic synthesis developed by Liu et al.,⁵⁹ where the aggregation of reactive sites facilitates the otherwise difficult-to-complete reactions.

According to the Winstein spectrum, polar additives/solvents would generally shift the equilibria to the right side with more disassociated species whereas aggregates of varying degrees of association are prevalent in nonpolar media. The proposed mechanism could thus be tested by performing the reaction in more polar solvent systems or in benzene with varying amounts of strong Lewis base since cross-association should be inhibited to a certain extent in both cases. To clearly reveal the role of cross-association, a ratio of 1:1 between PSLi and V8T8 was chosen so as to amplify the difference in the resulting product distribution. At this specific stoichiometry, the reaction in benzene yields predominantly star polymers with an average arm number of ~6 (Table 1) rather than a POSS-end-capped PS.

Scheme 2. (a) General Winstein Spectrum and (b) Proposed Mechanism Involving Cross-Association and Intra-Aggregate Addition



The solvent effect was first examined in three solvents, namely, benzene, benzene/THF mixed solvent ($v/v = 30/1$), and THF. The results (Figure 7a and Table 1) clearly indicate that the product distribution is very similar for the products obtained in benzene and in benzene/THF mixed solvent, both of which prefer higher addition products. In contrast, the reaction in pure THF yields a mixture of star polymers with a much lower average arm number of ~ 4.1 . Although the addition of ~ 10 equiv of THF (relative to PSLi concentration) has been known to be sufficient to break most of the aggregation between PSLi,⁵⁵ it does not seem to inhibit the cross-association completely. The strong tendency toward aggregation in benzene is probably due to the very high local charge densities in those higher addition products. The cross-association is only significantly inhibited in the complete absence of nonpolar solvents as in pure THF. Even in this case, the cross-association-promoted intra-aggregate addition and the usual stepwise addition are yet still in competition, trapping the products at multiple intermediate stages as demonstrated by the much decreased average arm number.

More evident results were obtained by performing addition reaction in the presence of a Lewis base additive, N,N,N',N' -tetramethylethylenediamine (TMEDA). TMEDA is one of the most strongly coordinating ligands and disassociating base for organolithium species⁶⁰ and has been extensively used in anionic polymerization to control the reactivity of the organolithium chain end.^{1,61} The result is shown in Figure 7b and Table 1. The addition of only 4 equiv of TMEDA effectively shifted the product distribution to those with much lower arm numbers (~ 2.2). Notably, with a large excess of TMEDA (70 equiv), the average arm number of the crude product (~ 1.2) is very close to what is expected from the feed ratio (1:1), suggesting that the cross-association should be almost completely inhibited in this case and the reaction should proceed mainly in a step fashion with the major product being the monoadduct. While it is difficult to estimate the relative

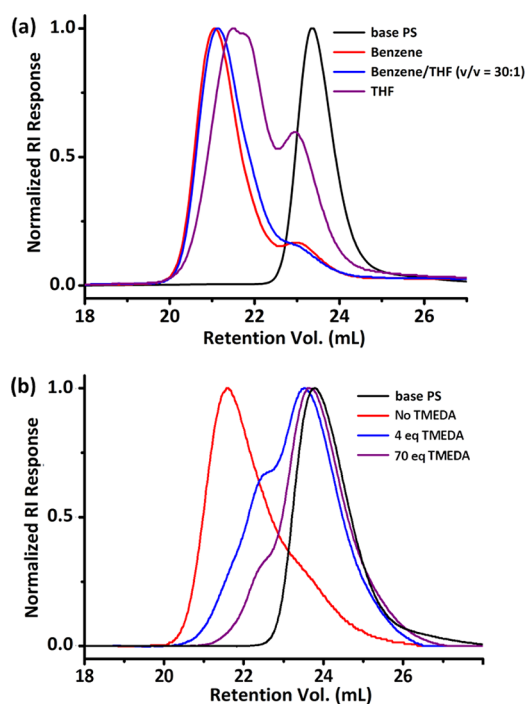


Figure 7. (a) SEC overlay of the base PS ($M_n = 4.4$ kg/mol, PDI = 1.02, black) and the crude product obtained after 30 min addition reaction in benzene (red), in benzene/THF ($v/v = 30/1$) mixed solvent (blue), or in THF (purple). (b) SEC overlay of the base PS ($M_n = 4.3$ kg/mol, PDI = 1.01, black) and the crude product obtained after 30 min addition reaction in benzene with 0 equiv of TMEDA (red), 4 equiv of TMEDA (blue), or 70 equiv of TMEDA (purple). All reactions were performed at a 1:1 ratio between PSLi and V8T8.

value of the kinetic constants for each step of the addition reactions, it is reasonable to conclude that the presence of nonpolar solvents promotes aggregation (both between living

polymers and between the addition intermediates and living polymers), which plays a crucial role in pushing the reaction to completion despite unfavorable stoichiometry.

CONCLUSIONS

In summary, a rapid and efficient anionic synthesis of well-defined eight-arm star polymers has been developed and found to be less sensitive to the molecular weight of the arm and the reaction stoichiometry. The method is based on the addition of poly(styryl)lithium to octavinylPOSS in nonpolar solvents such as benzene. With only slight excess of PSLi, the reaction proceeds rapidly to completion (within 5 min for MW of each arm up to 33 kg/mol), forming predominantly eight-arm star polymers. The products were purified by fractional precipitation and fully characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, FT-IR, MALDI-TOF mass spectrometry, and SEC. More strikingly, even at highly unfavorable stoichiometry for star polymer formation (such as 1:2 between PSLi and V8T8), the product distribution is still centered at higher addition product side. Such an unusual independency on stoichiometry is unprecedented in the synthesis of star polymers. A cross-association-promoted intra-aggregate addition mechanism was invoked to explain the experimental observation. As evidence, when the reaction was performed in a polar solvent, tetrahydrofuran, or when a strongly coordinating and disassociating Lewis base, tetramethylethylenediamine, was added to break the cross-association, star polymers were formed with lower average arm numbers than those of the products synthesized in pure benzene without additives at the same stoichiometry of the reactants. The method can be extended to other living anionic polymers, such as PBLi, PILi, and even polystyrene-*block*-polyisoprene living block polymers, for the preparation of miktoarm stars and block copolymer stars. While the tendency toward higher addition does seem to work against the synthesis of well-defined miktoarm stars, the combination of current method with other "grafting-to" methods such as hydrosilylation⁵¹ provides an alternate approach to do so. With the ease of operation and the high efficiency, the method has general implications in the understanding of the reactive nature of living polymeric anions and may find practical application in the synthesis of functional star polymers with diverse compositions and complex architecture.

ASSOCIATED CONTENT

Supporting Information

Addition characterization data such as the FT-IR and ^{13}C NMR data of the star PS; SEC result of one control experiment. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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