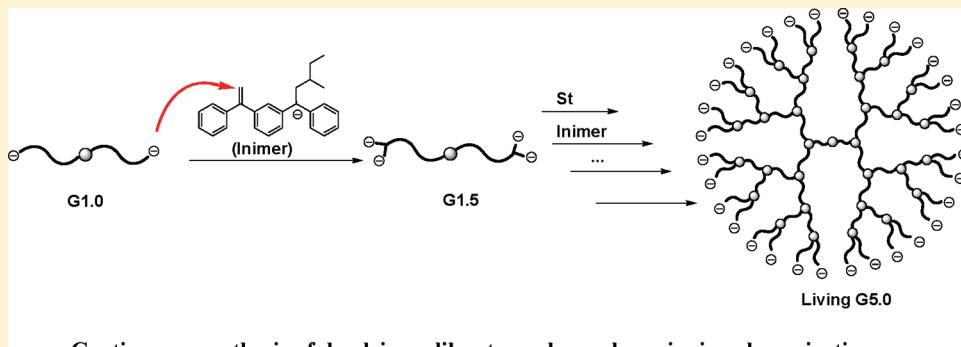


Continuous Process for the Synthesis of Dendrimer-Like Star Polymers by Anionic Polymerization

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Supporting Information



ABSTRACT: A continuous anionic living process for the fast synthesis of dendrimer-like star polymers is described. The process is based on the selective addition of *sec*-butyllithium (*s*-BuLi) toward 1,3-bis(1-phenylethenyl)benzene (MDDPE), which gives stoichiometric monoadduct in tetrahydrofuran (THF). The monoadduct, an anionic inimer-like molecule, is then used as the branching agent in the synthesis of dendrimer-like star polymers. Thus, α,ω -bifunctional polystyryllithium (G1.0), initiated by a difunctional anionic initiator, undergoes addition reaction with the monoadduct to form a tetrafunctional species, which is able to initiate the polymerization of styrene to form a four-arm star with terminal polystyryl anions (G2.0). Repeating addition/polymerization in an alternate way leads to the formation of a dendrimer-like star polystyrene up to the fifth generation, G5.0. The process is performed in a continuous way without separation of the intermediate species. The synthetic procedure of dendritic polystyrene is greatly accelerated, e.g., G5.0 with 32 terminal groups being obtained within 12 h. Because the product is living, it is employed as a dendritic precursor to prepare dendrimer-like star block copolymers such as PS-*b*-PI, PS-*b*-PMMA, and dendrimer-like star polymer with a graft-on-graft periphery. The solution properties of the dendrimer-like star products, such as viscosity as a function of molecular weight and globular shape, are investigated using viscometry and laser light scattering. The morphology of the individual molecules is observed using AFM and TEM.

INTRODUCTION

Dendrimer-like star polymers are a new class of dendrimers, in which successive generations are interlinked by polymer chains emanating radially from a central core.¹ These polymers have not only precise numbers of branching points and periphery functionalities, but also polymer segments with controlled lengths. As such, their properties are endowed with both the “dendrimer effect,” which provides a multiplicity of reactive sites and a reduced intermolecular entanglement, and the chemistry of specific polymers. In addition, the size of dendrimer-like star polymers spans a wide range from several to hundreds of nanometers, which is quite different from regular dendrimers.

In analogy to conventional dendrimers,^{2,3} dendrimer-like star polymers are prepared through either divergent or convergent approaches.⁴ In both approaches the polymer segments are formed either by *in situ* polymerization, or by presynthesized polymer precursors with terminal functionalities. The synthesis

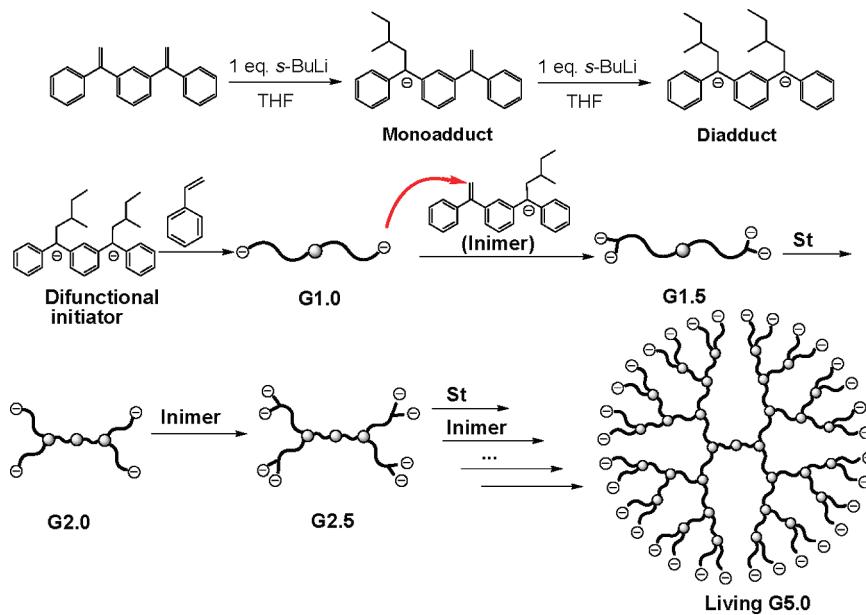
of dendrimer-like star polymers can be traced back to the seminal report on the synthesis of dendritic poly(ethylene oxide) (PEO) by Gnanou and co-workers using a divergent branching/polymerization approach.⁵ This strategy allows the syntheses of a series of dendrimer-like star PEOs,⁶ polystyrenes (PS),⁷ and dendrimer-like star block copolymers of EO/styrene,^{8–10} as well as styrene/*tert*-butyl acrylate (*t*BA)¹¹ with different block sequences, by employing living polymerization techniques such as atom transfer radical polymerization (ATRP) and anionic ring-opening polymerization (AROP). Incorporation of an ATRP initiating site at each branch point using a specific AB₂C-type branching agent enables the preparation of dendrimer-like star PEO bearing pH responsive poly(acrylic acid) (PAA) segments.¹² The divergent polymer-

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Scheme 1. Continuous Synthesis of Dendrimer-Like Star Living Polystyrene in a Divergent Process



ization approach has also been used to synthesize Janus-type dendrimer-like star PEOs, starting from a heterodifunctional initiator as the core.¹³ Recently, the same research group has explored a fast one-pot, two-step method to synthesize dendrimer-like star PEOs through a semicontinuous process, which does not require a protection/deprotection step, but only precipitation purification of the intermediate by using a commercially available glycidol as the branching agent.¹⁴ Hedrick is the first to give the name “dendrimer-like star polymers” to a series of dendritic poly(ϵ -caprolactone)s (PCLs) synthesized through ring-opening polymerization of caprolactone initiated by a multifunctional core, using protected 2,2-bis(phenyldioxymethyl)propionic acid (BMPA) as the branching agent.^{15–22} The terminal hydroxyl groups are further transformed into ATRP initiators, enabling the synthesis of dendrimer-like star block copolymers such as PCL-*b*-poly(methyl methacrylate) (PCL-*b*-PMMA),²³ and PHEMA-*g*-PEO.²⁴ In another elegant study, an array of constitutional isomers of dendrimer-like star PCLs are synthesized with varying placement of branching junctures, thus facilitating the relationship study of conformation and dendritic structure.¹⁹ Percec has developed a TERMINI (TERminator Multifunctional INIitiator) strategy to synthesize dendrimer-like star PMMAs in which metal-catalyzed living radical polymerization (LRP) of MMA is quantitatively and irreversibly interrupted by TERMINI, such as (1,1-dimethylethyl)[[1-[3,5-bi(S-phenyl-4-N,N'-diethylthiocarbamate)phenyl]ethenyl]oxy]dimethylsilane, a masked difunctional initiator for the subsequent LRP of MMA.^{25,26} The synthesis is efficient, and the products possess perfect structure due to the quantitative masking and demasking reactions of TERMINI.²⁷ Therefore, the divergent branching/polymerization approach, such as TERMINI methodology and highly efficient group modification, has been proved an efficient way to synthesize dendrimer-like star polymers.²⁸ Divergent branching/*in situ* polymerization strategy has also been successfully used in the synthesis of dendrimer-like star copolymers of styrene and L-lactide or carprolactone by sequential ATRP and ROP.^{29–31} Combination of ATRP and azide–alkyne click chemistry as the branching reaction has led

to the synthesis of dendrimer-like star PS and PS-*b*-PtBA (*co*)polymers of third generation.³²

A notable strategy in the synthesis of dendrimer-like star polymers is the use of living anionic polymerization. The advantage lies in the fact that the reactions of anionic species, especially carbanions, are well-known robust, orthogonal, and efficient (ROE) reactions.^{33,34} Carbanionic polymerization enables the design of dendrimer-like star polymers not only through divergent branching, but also through convergent coupling using a polymeric precursor. For instance, Hirao and co-workers has developed an iterative divergent methodology in which the generation growth is fulfilled by the coupling reaction of premade living PMMA chains bearing two functional groups of *tert*-butyldimethylsilyloxymethylphenyl (SMP) in the α -end, which are subsequently transformed into benzyl bromide before the attachment of the next generation.^{35–40} The generation growth is similar to the synthesis of regular dendrimers, albeit using polymeric (mostly PMMA) AB_n-type building blocks, so that the dendritic products are of high perfection. For example, dendrimer-like star PMMAs have been synthesized up to the seventh generation with well-controlled branching densities.^{41–45} Modification of the method facilitates the syntheses of a number of dendrimer-like star copolymers such as PMMA-*b*-PHEMA,³⁷ PMMA-*b*-PtBMA, PMMA-*b*-P2VP, PMMA-*b*-PDDMMA (poly((2,2-dimethyl-1,3-dioxolan-4-yl)methyl methacrylate)),⁴⁶ and PMMA-*b*-PS,⁴⁷ as well as dendritic-linear block copolymers of styrene and MMA.^{48,49}

Anionic polymerization also affords the convergent process in which alternate coupling of living polymeric precursors and subsequent polymerization initiated by the residual living center is performed to form dendrimer-like star structures. This has been achieved in the pioneering work by Hadjichristidis in the synthesis of dendritic homopolymers and copolymers of styrene and dienes, through a coupling reaction of “living stars” with chlorosilane derivatives.^{50,51} Knauss has developed a one-pot process for the dendritic polystyrene through a multibatch, stoichiometric addition of styrene and chlorosilane functionalized styrene (the branching agent) into a solution of

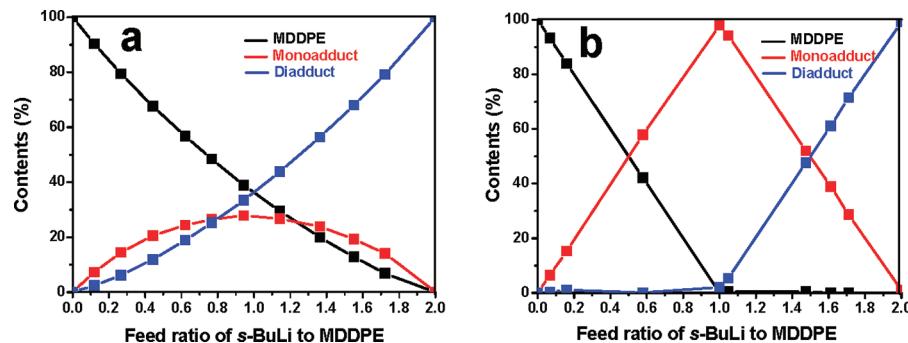
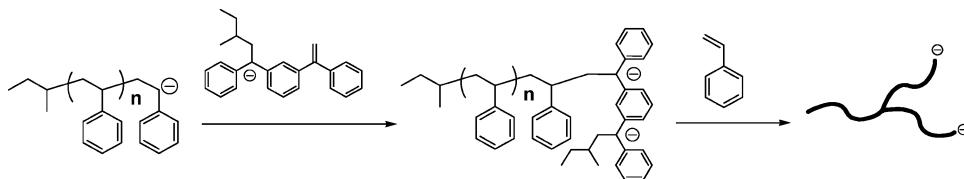


Figure 1. Variation of product distribution along with feed ratio of s-BuLi/MDDPE in the addition reaction in (a) cyclohexane at 45 °C and (b) in THF at ca. -80 °C.

Scheme 2. Model Reactions for the Branching Process



polystyryl anions.^{52–55} During the reaction, the chlorosilane moiety couples with living chains, while the vinyl group takes part in polymerization, thus forming a “T-shaped” branch juncture. Hutchings has synthesized dendrimer-like star polymers, such as the polystyrene DendriMacs, through convergent Williamson coupling of an AB₂-type polystyrene macromonomer prepared by anionic polymerization.⁵⁶ However, the coupling efficiency is influenced greatly by the solvent. Copper-catalyzed Huisgen dipolar cycloaddition, known as the “click” chemistry, affords higher coupling efficiency of corresponding polymer precursors with appropriate functionalities.^{57–61}

In both the divergent and convergent approaches, functionality transformations along with protection/deprotection processes are necessary to ensure a smooth switch between generations. These cascade processes are time-consuming. Although there have been a number of improved methods in the synthesis of regular dendrimers,^{33,34,62–64} to the best of our knowledge, the rapid synthesis dendrimer-like star polymers are limited to two cases. Dendrimer-like star PEOs was synthesized in a semicontinuous way by employing glycidol as the branching agent.¹⁴ Dendrimer-like star DNA up to fourth generation was synthesized through recognition-based divergent growth of Y-shaped DNA building blocks.^{65–67}

The chemistry of organolithium and 1, 3-bis(1'-phenylvinyl)-benzene (MDDPE) has long been used in macromolecular design through anionic polymerization. Depending on addition behavior of carbanions toward MDDPE, e.g., monoaddition or diaddition,^{68–82} a number of polymers with different architectures, such as ABA-type linear block,^{69,70} star-shaped,^{74–78} ring-shaped,^{79,80} and H/π-shaped polymers⁸¹ have been synthesized. McGrath⁸² observed high yield of monoadduct from the reaction of equivalent s-BuLi and MDDPE, but the reaction was never used for the design of polymer structures. In a previous work, we developed a solvent-switching method in which the monoadduct was able to be stored in cyclohexane (as a stock solution), providing a reliable handle of an anionic inimer to prepare hyperbranched polymers.⁷³ In the present work, we use the anionic inimer

as a branching agent to synthesize more regular dendrimer-like star polymers through the divergent branching/polymerization approach. Since the intermediate species is living, the process can be performed in a continuous way, thus greatly promoting the synthetic efficiency of dendrimer-like star polymers.

RESULTS AND DISCUSSION

The overall route for continuous synthesis of dendrimer-like star polymers is outlined in Scheme 1. The synthesis starts with styrene polymerization initiated by a difunctional anionic initiator, e.g., the diadduct of s-BuLi with MDDPE. The resulting α,ω-difunctional polystyryllithium is coded G1.0, the first generation. G1.0 is then reacted with an anionic inimer, e.g., the monoadduct of s-BuLi and MDDPE, yielding an α,α',ω,ω'-tetrafunctional polystyryllithium, coded G1.5. Further polymerization of styrene initiated by G1.5 results in the formation of G2.0. Repeating the process of inimer addition and initiation-polymerization will finally lead to dendrimer-like star polymers up to high generations.

There are two key steps in the synthesis: (i) the selective addition of s-BuLi toward MDDPE, which ensures the synthesis of pure anionic inimer and dilithium initiator; (ii) the branching reaction which is composed of stoichiometric addition reaction of polystyryllithium (PSLi) toward the anionic inimer, and the subsequent initiation of styrene polymerization by the resulting dianion. These reactions will be separately discussed in detail in the following sections.

Selective Addition of s-BuLi toward MDDPE. The addition reaction of s-BuLi toward MDDPE is well documented in the literature. The earlier reports show that the two vinyl groups are equivalent to anionic addition.^{82–85} Therefore, monoadduct was obtained usually by using excessive MDDPE in the reaction.^{85,86} Nevertheless, the addition behavior seems to be remarkably different between cyclohexane and THF as the solvent.⁸² As shown in Figure 1, in cyclohexane the product is always a mixture of monoadduct and diadduct. The monoadduct never exceeds 50% content, indicating comparable addition rate of the two double bonds. In THF the monoadduct is obtained in high yield (96% by HPLC and

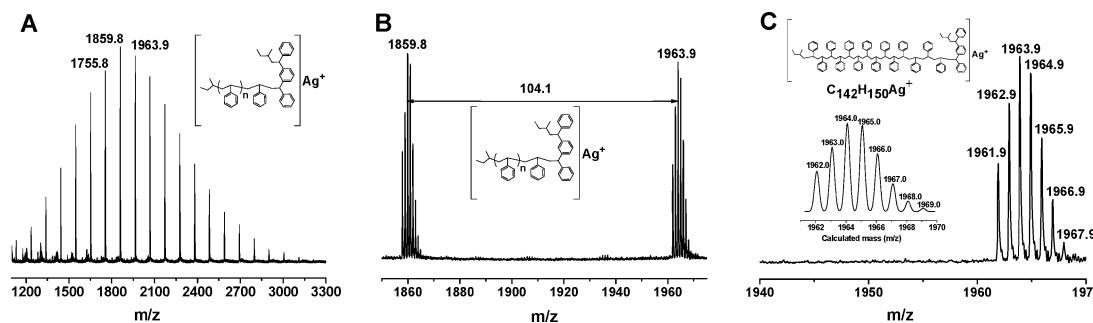


Figure 2. MALDI-TOF MS spectrum of the adduct of polystyryllithium and the inimer: (A) full spectrum, (B) enlarged part, and (C) calculated (inset) and observed isotope peaks.

GC) when the feed amounts of the reactants are equal in mole, while the diadduct is obtained in high yield from the double molar ratio of *s*-BuLi to MDDPE. This striking result stems from the electrostatic repulsion between the carbanion in the formed monoadduct and the approaching anion of *s*-BuLi, prohibiting the addition of the second molecule of *s*-BuLi.^{82,85–87} In THF, carbanions are more naked due to the solvation of the counterion, imparting larger electrostatic repulsive force than that in cyclohexane.

The addition reaction in THF is completed within 15 min at ca. –80 °C. After the reaction, the solvent is switched from THF to cyclohexane by distillation. Both the monoadduct and the diadduct form a homogeneous solution in cyclohexane, which are used as stock solution of inimer and dilithium initiator, respectively. The characterization of the monoadduct has been performed as previously discussed.⁷³

The Branching Reaction. The efficiency of branching reaction is investigated through a model reaction (Scheme 2). First, the addition of polystyryllithium to the inimer is performed in cyclohexane using a linear polystyryllithium (M_n , SEC = 1600 g/mol), resulting in a polystyryl α,α' -dianion (M_n , SEC = 2000 g/mol). MALDI-TOF MS spectrum of the product is shown in Figure 2, in which the main series is assignable to the inimer-capped species. For instance, the peak at m/z = 1963.9 is assigned to species with a degree of polymerization, DP = 14 ($104.1 \times 14 + 57.1 \times 2$ (two butyl) + 282.4 (MDDPE) + 107.8 (Ag) + 2.0 (two hydrogens) = 1963.8).

Second, the dianionic adduct is used to initiate the polymerization of styrene to form a star-like product. SEC trace shifts clearly to larger molecular weight, as shown in Figure 3. The SEC measured molecular weight, 7800 g/mol, is notably smaller than that measured by multiangle laser light scattering (MALLS), 9600 g/mol, indicating a nonlinear architecture of the polymerization product after the cross-initiation. The initiation capability correlates well with previous successful access to MDDPE-derived dilithium initiators for the synthesis of SBS block copolymers^{68–70} and cyclic polymers.^{77,78}

Synthesis of Dendrimer-Like Star Polystyrene. The overall synthetic process of dendrimer-like star polystyrene involves essentially multistep of the two elementary reactions in the model branching process, performed by alternate charge of the stock solution of inimer and styrene without isolation of the intermediate species. This continuous approach, starting from the polymerization of styrene initiated by the diadduct, affords dendrimer-like star polystyrene up to the 5.0th generation within 12 h. Within each generation the molar ratio of monomer to organolithium is kept constant so as to obtain

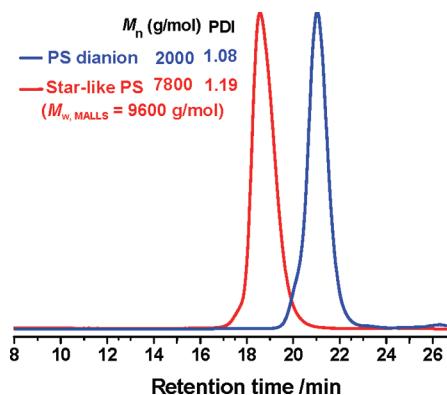


Figure 3. SEC chromatograms tracing the model branching reaction. Key: blue line, adduct of polystyryllithium with the inimer; red line, star-like polystyrene initiated by the adduct dianion.

identical chain length among generations, $M_{n,arm}$. The results of two polymerization systems with different $M_{n,arm}$ are listed in Table 1. Samples are taken for analysis after each step of the reaction. ¹H NMR is used to follow the alkyl diphenyl methine protons derived from the terminated MDDPE moieties. As shown in Figure 4, these protons give a multiplet at δ ~4.0 ppm for the starting diadduct, but show broad signals at δ ~3.9 ppm for those intermediate species with terminal MDDPE-derived moieties (G1.5–G3.5). The methine signal disappears in the spectra of samples after the subsequent polymerization (G1.0–G4.0), indicating rather efficient cross initiation. It is also noted that the intensity of methine signal becomes weaker along with the generation growth, and is undetectable for G4.5, due to decreasing content of the terminal MDDPE-derived moiety in the whole molecule. Backfolding of the periphery groups into the inner part of the dendritic structure may also reduce the intensity of methine signal.

Much attention should be paid to the formation of pseudogel during the process. The pseudogel is a physical network formed by the aggregation of polymeric anions, and is often encountered in the preparation of bi- and multifunctional organolithium species.^{28,73} Once it gels, the solution becomes heterogeneous with high viscosity, which impedes further stirring and reaction. It is observed that the pseudogel formation relates to two factors: the arm length, $M_{n,arm}$, and the structure of periphery anions. Longer arm length leads to earlier gelation. For instance, in the presence of small amount of THF, pseudogel appears at G4.5 when the arm length is 6000 g/mol, whereas earlier gelation at G3.5 is observed for the system with arm length of 12000 g/mol. Usually, the pseudogel formed with periphery polystyryl anions become fluidic upon

Table 1. Synthesis and Characterization of Dendrimer-Like Star Polystyrenes

samples	$M_{n,\text{calc}}$ (10^3 g/mol)	$M_{n,\text{SEC}}$ (10^3 g/mol)	$M_{w,\text{MALLS}}$ (10^3 g/mol)	PDI _{SEC}	$[\eta]_w^b$ (mL/g)	g^c	dn/dc	R_h^d (nm)	R_g^e (nm)	R_g/R_h
G1.5-PS ₂₇₀₀ ^a	5.7	6.5	6.8	1.21	8.5	1.09	0.194	/	/	/
G2.5-PS ₂₇₀₀	16.5	15.6	16.9	1.26	12.4	0.84	0.197	/	/	/
G3.5-PS ₂₇₀₀	38.1	30.8	38.0	1.40	24.5	0.94	0.194	5.6	/	/
G4.5-PS ₂₇₀₀	81.3	42.7	73.3	1.46	31.0	0.75	0.198	6.7	/	/
G5.0-PS ₂₇₀₀	167.7	70.4	131.0	1.52	33.1	0.53	0.187	8.7	14.7	1.7
G1.5-PS ₄₃₀₀	8.9	10.6	11.0	1.21	13.7	1.26	0.181	3.3	/	/
G2.5-PS ₄₃₀₀	26.1	22.7	24.1	1.28	25.2	1.33	0.198	4.5	/	/
G3.5-PS ₄₃₀₀	60.5	42.6	52.2	1.26	37.8	1.16	0.205	6.5	/	/
G4.5-PS ₄₃₀₀	129.3	62.0	107.0	1.40	41.8	0.78	0.197	8.9	15.4	1.7
G5.5-PS ₄₃₀₀	266.9	103.0	223.2	1.50	40.9	0.45	0.198	18.9	26.7	1.4

^aG1.5-PS₂₇₀₀ refers to dendritic product of generation 1.5 with the molecular weight between successive generations, $M_{n,\text{arm}} = 2700$ g/mol. ^bWeight-average intrinsic viscosity measured by online viscometry detector, Viscostar (Wyatt). ^cContraction factor $g' = [\eta]_w$ (dendrimer-like)/ $[\eta]_{\text{linear}}$, where $[\eta]_{\text{linear}} = 1.62 \times 10^{-2} M_w^{0.70}$.^{73,91} ^dDetermined by dynamic light scattering at a scattering angle of 90° in THF at 30 °C. ^eDetermined by static light scattering in THF at 30 °C.

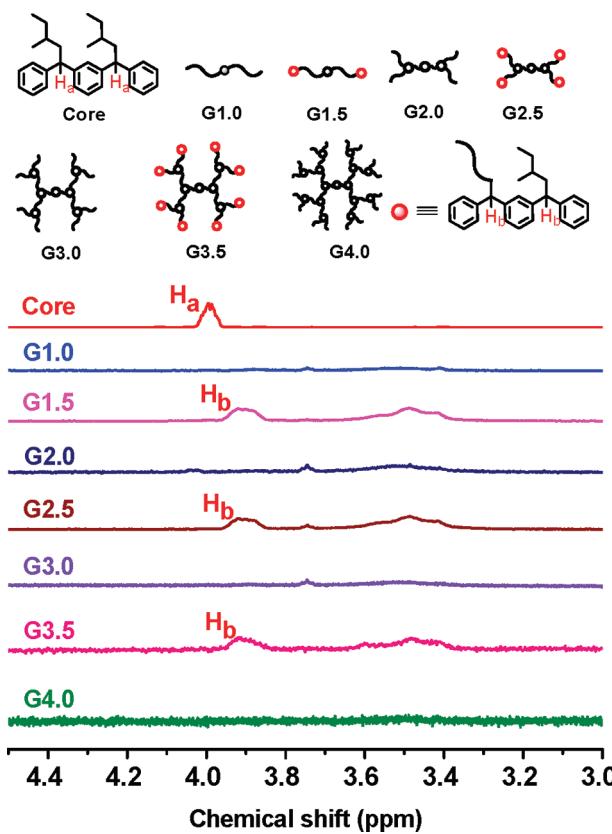


Figure 4. ¹H NMR spectra monitoring the synthesis of dendrimer-like star polystyrene up to the fourth generation. The spectra are obtained in CDCl₃ with the same concentration, showing only the part between chemical shifts of 3.0–4.5 ppm.

addition of inimer. This phenomenon is most likely related to different aggregation number of the terminal groups. Polystyryl anions aggregate into dimers,⁸⁸ whereas MDDPE-derived dianions may exhibit a fractional aggregation number less than two.

In order to avoid the pseudogelation in the whole process, polar additives such as ether and TMEDA are employed without changing the main solvent, cyclohexane. The abilities of these additives to dissociate the gel are as follows (at 1.0–2.0 equiv of Li): TMEDA > THF > ethyl ether. In the presence of ether, the pseudogel appears in the second generation, while THF is able to keep the reaction mixture homogeneous up to

the fourth generation. TMEDA is the most effective, whereby the pseudogel does not appear in the whole procedure. However, the molecular weight distribution is broader possibly due to the slow initiation of MDDPE-derived dianion in the presence of TMEDA. Therefore, THF is used in lower generations, and TMEDA for the highest generation. The presence of trace amount of polar additives does not have a significant effect upon the addition reaction.

As the reaction proceeds in a proliferative manner, the feed amounts of inimer and monomer will be doubled in each follow-up step. This will cause difficulty in experimental manipulation. Therefore, the reaction mixture is divided into two parts of equal volume at each step, only one of which is subjected to the subsequent reaction after being diluted with equal volume of solvent.

Figure 5 shows the SEC traces of the fractionated polymerization products with increasing generations. The

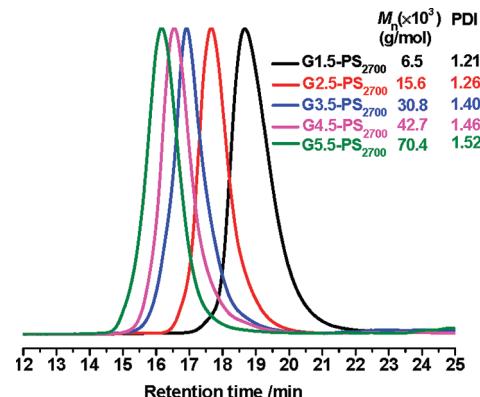
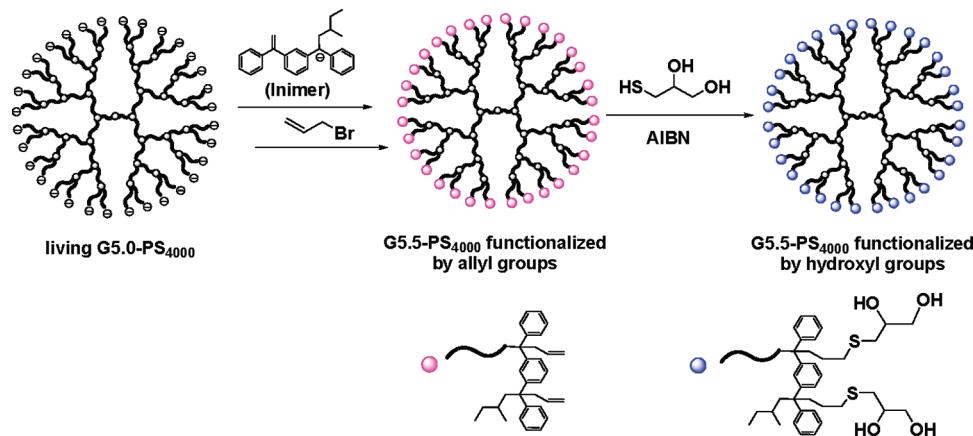


Figure 5. SEC traces monitoring the synthesis of dendrimer-like star polymers of G1.5 to G5.5 with the arm length of 2700 g/mol (samples are fractionated from toluene/methanol).

molecular weight shifts clearly to larger values while remaining monomodal distribution. The characterization data in Table 1 show that the molecular weights, $M_{n,\text{SEC}}$, are remarkably lower than the calculated, $M_{n,\text{calc}}$, due to smaller hydrodynamic volume of dendritic polymers. The latter is close to those measured by MALLS, $M_{w,\text{MALLS}}$. The polydispersity index measured by SEC varies from 1.2 for G1.5-PS₂₇₀₀, to 1.5 for G5.0-PS₂₇₀₀. These relatively broad values indicate the existence of defects in the dendrimer-like star structures. The

Scheme 3. Functionalization of Living G5.5-PS₄₀₀₀ with Allyl and Hydroxyl Peripheral Groups

degree of the perfection is therefore estimated in terms of the terminal or peripheral groups of the dendritic products after functionalization with allyl bromide. In order to avoid the potential lithium-halide exchange reaction, only inimer-capped living products are reacted with allyl bromide, as shown in Scheme 3.

The ¹H NMR spectrum of the functionalized product, G5.5-PS₄₀₀₀-vinyl with molecular weight of polystyrene between successive generations, $M_{n,\text{arm}} = 4000 \text{ g/mol}$, is shown in Figure

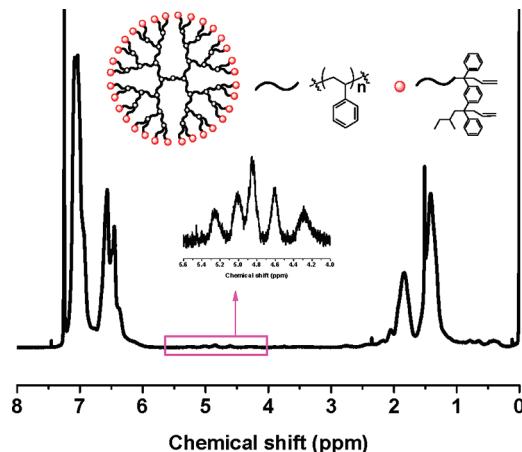


Figure 6. ¹H NMR spectrum of the G5.5-PS₄₀₀₀-vinyl with peripheral allyl functionality (in CDCl₃).

6. The peaks between $\delta = 4.0$ to 5.4 ppm are assigned to vinylic protons. Nevertheless, these signals are too weak to provide convincing information on the end functionality. Therefore, the content of the vinyl groups are analyzed via iodometric titration (IBr/KI/Na₂S₂O₃²⁻), and the results are listed in Table 2. It is

obvious that for samples of lower generations, a fair to good agreement between measured and anticipated number of peripheral vinyl functionalities is observed, but deviation is notable for higher generations. For instance, a number of 64 vinyl groups are expected for G5.5-PS₄₀₀₀-vinyl, whereas an average of 53.5 is measured. Thus, defects indeed exist in the dendrimer-like star products, possibly due to the incomplete addition and cross initiation. Furthermore, the experimental error in quantifying the reactants, such as the inimer, may also cause defects in the final products.

Solution Properties of Dendrimer-Like Star PS. One of the features that distinguish dendritic polymers from their linear counterparts is the dependence of intrinsic viscosity, $[\eta]$, on molecular weight. While the $[\eta]$ of linear polymers is expressed as a power law function of molecular weight, according to Mark–Houwink–Sakurada equation, the regular dendrimers usually show parabolic variations of $\log[\eta]$ as a function of generation or molecular weight, due to the gradual transition from open structure to compact globular form along with increasing generations. Dendrimer-like star polymers have a lower degree of branching compared to regular dendrimers, and thus have a less compact chain density in solution. Nonetheless, the same trend in viscosity variation with increasing generation should still hold for dendrimer-like star polymers. Gnanou and co-workers were the first to report similar behavior in the generation dependence of viscosity.^{7,28} They also pointed out that in some cases, a level-off of the curve $\log[\eta] \sim \text{generation}$ was observed because the maximum of viscosity may be shifted to generations higher than actually measured.⁶ Figure 7 shows the weight-average intrinsic viscosity, $[\eta]_w$, against molecular weight in double-logarithm scale for dendrimer-like star products possessing two different chain lengths between successive generations ($M_{n,\text{arm}}$). The intrinsic viscosity initially increases with molecular weight, but

Table 2. Results of Estimation of Number of Peripheral Groups by Allylic Functionalization

samples	M_n, calc (10^3 g/mol)	M_n, SEC (10^3 g/mol)	M_w, MALLS (10^3 g/mol)	PDI _{SEC}	$N_{\text{allyl},\text{theor}}^a$	$N_{\text{allyl},\text{obs}}^b$
G1.5-PS ₄₀₀₀ -vinyl	8.4	9.0	8.8	1.19	4	3.8
G2.5-PS ₄₀₀₀ -vinyl	24.4	20.6	25.2	1.22	8	7.0
G3.5-PS ₄₀₀₀ -vinyl	56.4	30.8	54.0	1.30	16	14.2
G4.5-PS ₄₀₀₀ -vinyl	120.4	52.0	113.5	1.45	32	26.5
G5.5-PS ₄₀₀₀ -vinyl	248.4	79.0	255.0	1.52	64	53.5

^aTheoretical number of vinyl groups in the periphery was calculated by $N_{\text{allyl},\text{theor}} = 2^{G+0.5}$, in which G is the number of generation. ^bObtained by iodometric titration using IBr.

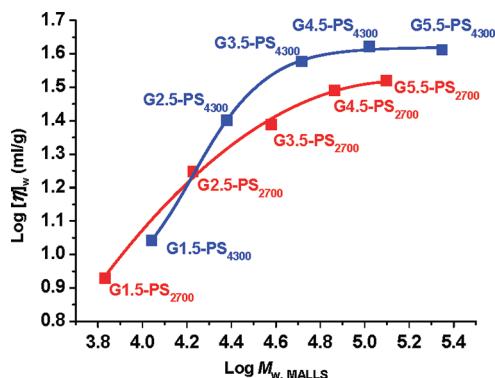


Figure 7. Dependence of intrinsic viscosity on molecular weight in double logarithmic style for dendrimer-like star polymers with various generations.

then reaches a level-off region, indicating a gradual transition from open structures of the first to third generations, to more compact globular conformation of the fourth and fifth generations.^{3,89} Nevertheless, we do not observe the inflection point on $[\eta]_w$ as a function of molecular weight, as is usually observed for regular dendrimers. This implies that the tightest compact form is not yet reached at the fifth generation. The samples with lower $M_{n,arm}$ show lower intrinsic viscosities due to the higher degrees of branching. In addition, the intrinsic viscosities measured for the dendritic samples are remarkably lower than those of linear polystyrene. The contraction factor, g' , defined the ratio of viscosities of dendritic samples to their linear counterparts of identical molecular weight, decreases from 1.09 to 0.53 along with the generation increase (Table 1).

The size and shape of the dendritic products in THF are investigated using static light scattering (SLS) and dynamic light scattering (DLS). SLS is performed either on MALLS in an off-line mode or on an ALV instrument. The radius of gyration, R_g , is measured to be 26.7 nm for the sample with the highest generation, G5.5-PS₄₃₀₀. For other samples, the signal-to-noise is too low to give accurate values of R_g because of the small size. Hydrodynamic radius, R_h , is determined by DLS at the scattering angle of 90° (Table 1). As shown in Figure 8, the profiles show monomodal distribution from G1.5 to G4.5-PS₄₃₀₀. The peak for G5.5-PS₄₃₀₀ is broad, possibly because of the intermolecular coupling, which may occur easily due to the multiplicity of the peripheral anions. The measured R_h increases along with molecular weight and generation. Good linearity between log R_h and log M_w is observed from G1.5 to G4.5-

PS₄₃₀₀, but deviation in G5.5-PS₄₃₀₀ is notable due to the presence of coupled species.

The globular shape of the dendrimer-like star polystyrene in THF is confirmed by DLS measurement on G3.5-PS₄₃₀₀ at different scattering angles, a method used by Gnanou and co-workers.¹² As shown in Figure 9, CONTIN analysis gives

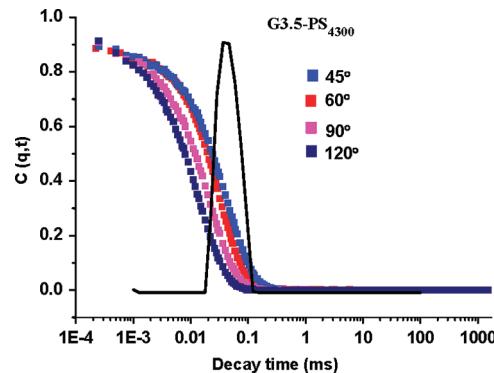


Figure 9. DLS results of dendrimer-like star polystyrenes of G3.5-PS₄₃₀₀ at different angles (in THF, at 30 °C).

narrow, monomodal distribution which is independent of the scattering angles, indicating that the dendrimer-like star polystyrenes molecules adopt a globular conformation in solution. Nonetheless, the ratios of R_g/R_h for G4.5-PS₄₃₀₀, G5.5-PS₄₃₀₀, and G5.0-PS₂₇₀₀ are 1.7, 1.4, and 1.7, respectively, which fall into the category for open structure,^{92,93} and are quite close to the result by Gnanou on dendrimer-like star PEOs.⁶

Microscopic Observation of Dendrimer-Like Star PS.

Single molecular morphology of dendrimer-like star polymers is investigated using AFM and TEM. AFM observations are performed by tapping mode for samples spin-coated on freshly cleaved mica from highly dilute solutions. Figure 10 shows the height image of G5.5-PS₄₃₀₀, in which single molecules are observed as scattered particles. The diameters and the heights of the particles are ca. 45 and 1.3 nm, respectively. The diameter is slightly larger than the R_h in solution (Table 1) while the height is strikingly small. This demonstrates that the dendrimer-like star products adopt a dome-like, flattened morphology on mica surface. Fine structures such as the branching points are invisible due to coiled conformation of polystyrene segments. The size of morphology observed by

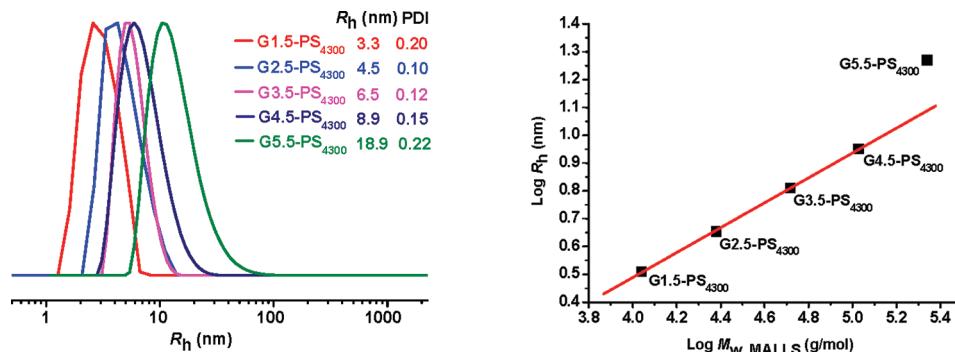


Figure 8. Profiles of DLS of dendrimer-like star polystyrenes from G1.5-PS₄₃₀₀ to G5.5-PS₄₃₀₀ (left), and the obtained R_h s as a function of M_w , MALLS in double logarithmic style (right).

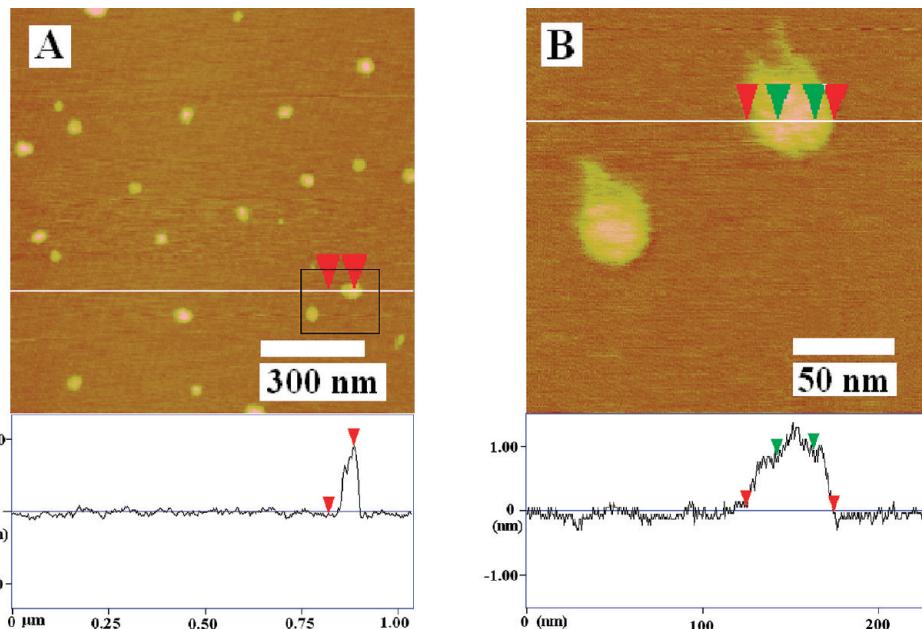


Figure 10. AFM images of G5.5-PS₄₃₀₀ obtained in tapping mode. The sample is spin-coated on mica from dilute CHCl₃ solution.

TEM (Figure 11) agrees well with AFM results, with a homogeneous circular profile after collapse on the copper grid.

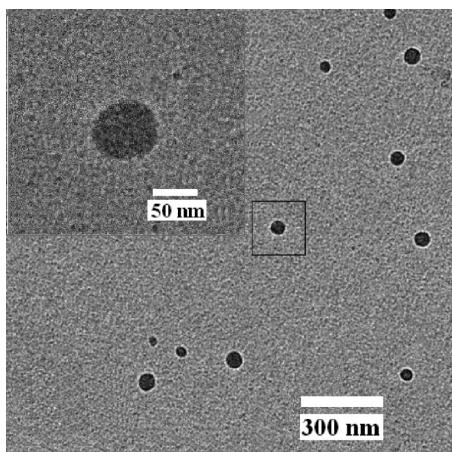


Figure 11. TEM image of G5.5-PS₄₃₀₀ deposited on a copper grid from dilute THF solution. The inset in red frame is the partial enlargement indicated in the figure.

The Application of Living Dendrimer-Like Star Polystyrene as the Precursor Building Block in Further Molecular Design. One of the attributes of the present method is that the product is living, and can be functionalized through anionic reaction or copolymerization. As an illustration, living dendrimer-like star polystyrene of the G5.5-PS₄₀₀₀ is functionalized with multiple periphery hydroxyl groups through sequential nucleophilic reaction with allyl bromide and thiol–ene reaction with 1-thioglycerol, as shown in Scheme 3.

Figure 12 shows the ¹H NMR result of the hydroxyl functionalized product. The protons of peripheral groups derived from 1-thioglycerol are clearly observed as signals at $\delta = 3.61$ (CH₂OH) and 3.74 (CHOH) ppm. From the integration the hydroxyl functionality is estimated to be 60.1, which is much lower than the anticipated hydroxyl functionality, 128, as

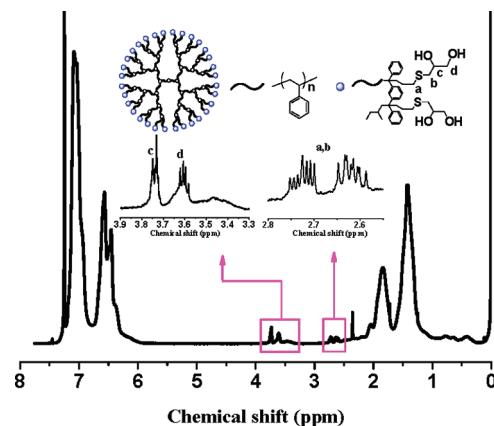


Figure 12. ¹H NMR spectrum (in CDCl₃) of G5.5-PS₄₀₀₀-vinyl after thiol–ene reaction.

well as the value determined by titration using a cyclohexane solution of 1, 1-diphenylhexyllithium (adduct of s-BuLi with 1,1-diphenylethylene), 92.7.

Dendrimer-like star block copolymers are synthesized via anionic polymerization of isoprene or methyl methacrylate (MMA) initiated by the dendritic polystyrene precursor end-capped with the inimer, e.g., G3.5-PS₃₃₀₀, as shown in Scheme 4. The polymerization of isoprene is performed in cyclohexane in the presence of trace amount of THF and TMEDA (polar additives used to destroy pseudogel as mentioned above), while MMA is polymerized in THF/cyclohexane (3:1) at low temperature. Both of the products, G4.0-PS-*b*-PI and G4.0-PS-*b*-PMMA, are easily fractionated from toluene/methanol to give monodisperse products (Figure 13).

Figure 14 shows the ¹H NMR spectra of the dendritic block copolymers after purification. It is obvious that the PI segment contains high percentage of 1,2- and 3,4-enchainment (69% and 11%, respectively) due to the presence of polar additives. The molecular weights and compositions of the dendritic block copolymers are listed in Table 3.

Scheme 4. Synthesis of Dendrimer-Like Star Block Copolymers

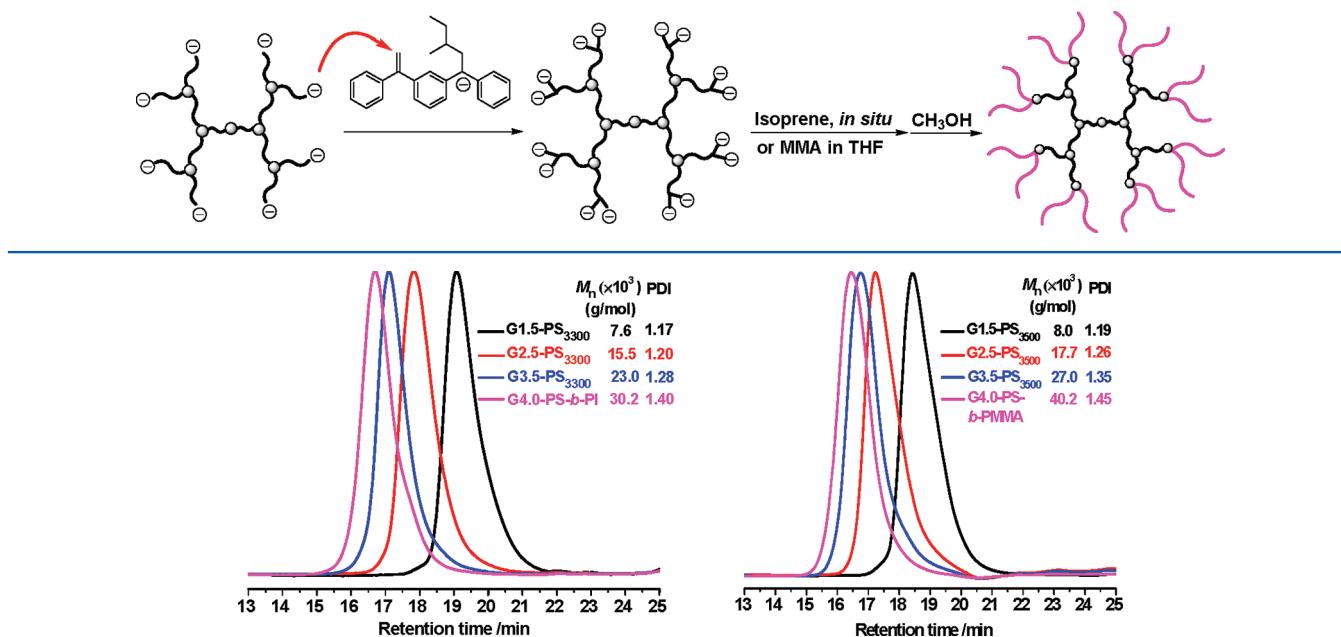
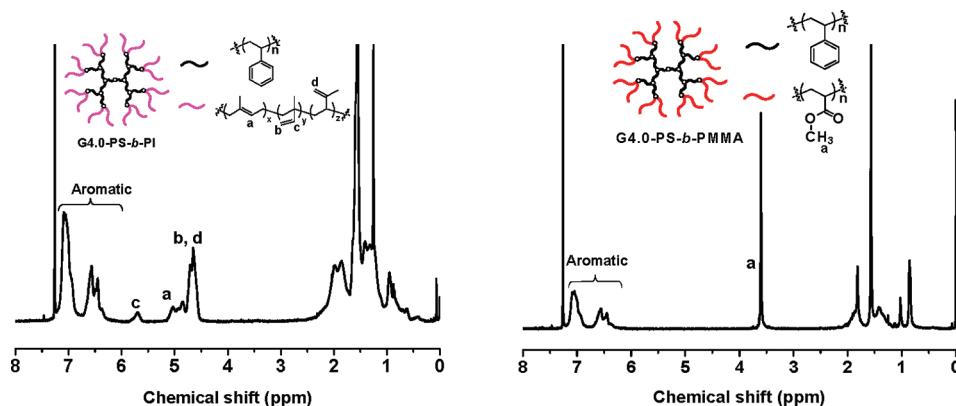
Figure 13. SEC curves tracing the synthesis of dendrimer-like star block copolymers, G4.0-PS-*b*-PI (left) and G4.0-PS-*b*-PMMA (right) (samples are fractionated from toluene/methanol).Figure 14. ^1H NMR spectra (in CDCl_3) of dendrimer-like star block copolymers, G4.0-PS-*b*-PI (left) and G4.0-PS-*b*-PMMA (right).

Table 3. Synthesis of Dendrimer-Like Star Block Copolymers and Dendrigrafts

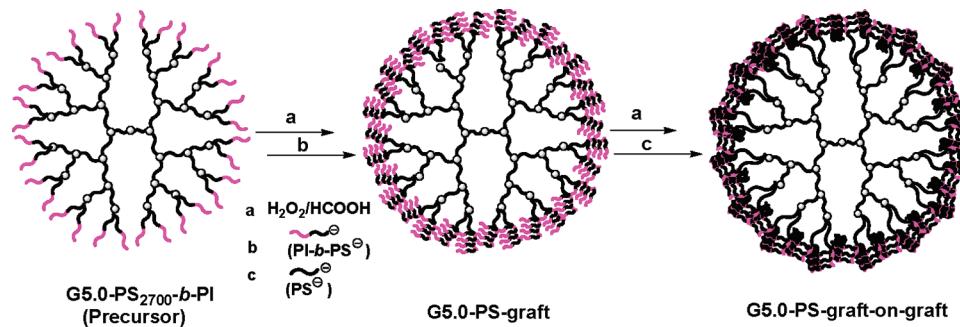
samples	$M_{n,\text{SEC}}$ (10^3 g/mol)	$M_{w,\text{MALLS}}$ (10^3 g/mol)	PDI _{SEC}	dn/dc	PS (%) _{theor} (in mol)	PS (%) from NMR (in mol)		
G3.5-PS ₃₃₀₀ (precursor)	23.0	45.0	1.28	0.190	/	/		
G4.0-PS- <i>b</i> -PI	30.2	71.2	1.47	0.136	54	55		
G3.5-PS ₃₅₀₀ (precursor)	27.0	55.3	1.35	0.190	/	/		
G4.0-PS- <i>b</i> -PMMA	40.2	96.8	1.52	0.112	67	60		
	$M_{n,\text{SEC}}$ (10^3 g/mol)	$M_{w,\text{MALLS}}$ (10^3 g/mol)	PDI _{SEC}	dn/dc	R_g (nm)	R_h (nm)	R_g/R_h	N_{arm}^d
G5.0-PS ₂₇₀₀ - <i>b</i> -PI ^a (precursor)	135	230	1.41	0.163	/	/	/	/
G5.0-PS-graft ^b	300	882	1.33	0.145	23.5	18.5	1.3	~300
G5.0-PS-graft-on-graft ^c	484	1840	1.21	0.173	25.2	24.5	1.1	850

^aG5.0-PS₂₇₀₀-*b*-PI is the product of isoprene polymerization initiated by living G5.0-PS₂₇₀₀ *in situ*. ^bPI₁₀-*b*-PS₁₀Li was used as the arm. ^cPSLi ($M_n = 1100$ g/mol) was used as the arm. ^dNumber of arms in periphery calculated from $M_{w,\text{MALLS}}$.

Dendrimer-like star block copolymer, G4.0-PS-*b*-PI, is used to prepare dendrimer-like star polymers with a dendrigraft periphery, a structure resembling “dendritic box” as reported by Meijer and co-workers.⁹⁰ The dendrimer-like dendrigrafts are synthesized through polymer grafting to PI segments (Scheme 5). Thus, living G5.0-PS₂₇₀₀ is used as a dendritic initiator to

initiate the polymerization of isoprene to give G5.0-PS₂₇₀₀-*b*-PI ($M_{w,\text{MALLS}} = 2.3 \times 10^5$ g/mol, molar percentage of isoprene units: 44%). The PI segment is then epoxidized by H₂O₂/formic acid in toluene, followed by grafting of a living diblock copolymer, PI₁₀-*b*-PS₁₀Li (polyisoprene-*b*-polystyryllithium, total $M_n = 1700$ g/mol, the subscripts refer to the individual

Scheme 5. Synthetic Route of Dendrimer-Like Star Polymer with a Graft-on-Graft Periphery



degree of polymerization), to prepare the first generation of dendrigrafts, **G5.0-PS-graft** ($M_w, \text{MALLS} = 8.82 \times 10^5 \text{ g/mol}$, molar percentage of isoprene units: 35%). Further grafting of PSLi ($M_n = 1100 \text{ g/mol}$) onto the PI segment of $\text{PI}_{10}-b-\text{PS}_{10}$ side chains in **G5.0-PS-graft** affords a graft-on-graft structure, **G5.0-PS-graft-on-graft** ($M_w, \text{MALLS} = 1.84 \times 10^6 \text{ g/mol}$, molar percentage of isoprene units: 11%). The results are shown in Figure 15 and Table 3. The PDI becomes narrower after the

CONCLUSIONS

The inimer-like monoadduct of stoichiometric reaction in THF between *s*-BuLi and MDDPE can be used as an efficient anionic chain branching agent. A continuous methodology is therefore developed for the synthesis of dendrimer-like star polymers using the monoadduct as the branching agent. The procedure involves alternate feeds of monomer and inimer into the reaction flask, with the aid of polar additives but without need for separation and purification of the intermediate generations. The synthetic efficiency is greatly promoted. To the best of our knowledge, this is the first truly continuous process in the synthesis of well-defined dendrimer-like star polymers.

Since the product is living, it is used as a precursor to synthesize dendrimer-like star polymers with peripheral functionalities and dendrigrafts, as well as dendrimer-like star block copolymers. We believe that this process can serve as a platform to synthesize a new class of dendrimer-like star polymers.

EXPERIMENTAL SECTION

Materials. Styrene (National Pharmaceutical, $\geq 99\%$), isoprene (TCI, $\geq 99\%$), methyl methacrylate (MMA) (TCI, $\geq 99\%$), and 1,1-diphenylethylene (DPE) (TCI, $\geq 99\%$) were distilled over CaH_2 and stored at -10°C . Styrene and isoprene were distilled over di-*n*-butylmagnesium (MgBu_2) (Aldrich, 1.0 M in heptane) on the vacuum line and MMA was distilled over tri-n-octylaluminium (Aldrich, 0.3 M solution in heptane) before use. Cyclohexane and tetrahydrofuran (THF) were refluxed over sodium with benzophenone as indicator, and distilled from 1, 1-diphenylhexylolithium (DPELi, adduct of *s*-BuLi with DPE) on the vacuum line before use. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) (Aldrich, $> 99\%$) was purified by distilling from DPELi in a vacuum line and stored at -10°C . *n*-Butyllithium (*n*-BuLi) (Aldrich, 2.5 M solution in cyclohexane/heptane) and methylolithium (Acros, 1.6 M solution in diethyl ether) were used as received. *sec*-Butyllithium (*s*-BuLi) (Aldrich, 1.3 M solution in cyclohexane) was titrated before use. Methyltriphenylphosphonium bromide (Lancaster, $> 98\%$) and 1, 3-dibenzoylbenzene (Aldrich, 98%) were vacuum-dried at 50°C for 24 h. MDDPE was synthesized according to previous method.⁹⁴

Measurements. High performance liquid chromatography (HPLC) was performed on an instrument composed of a Waters S15 pump, a C-18 column (Symmetry Shield RP-18, 5.0 μm , 4.6 \times 250 mm), and a UV-detector (254 nm). Acetonitrile/water (83/17, v/v) was used as eluent (1.0 mL/min) at 40°C . ^1H NMR and ^{13}C NMR measurements were carried out on a Bruker (500 MHz) NMR instrument, using CDCl_3 as the solvent and tetramethylsilane as the interior reference. Gas chromatography/mass spectroscopy (GC-MS) was performed on a Finnigan Voyager instrument in electron impact mode (70 eV). Size exclusion chromatography (SEC) analysis was performed through three Waters Styragel columns (pore size 10^2 , 10^3 , and 10^4 \AA), calibrated by narrow polystyrene standards, and equipped with three detectors: a DAWN HELEOS (14–154°) (Wyatt

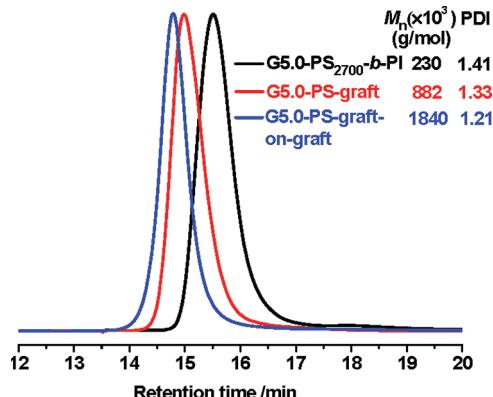


Figure 15. SEC results of dendrimer-like star polymer with graft-on-graft periphery after fractionation from toluene/methanol.

grafting reaction, decreasing from 1.41 in precursor to 1.33 and 1.21 after first and second grafting reactions, respectively. The grafting reaction is also confirmed by ^1H NMR (Figure S7, Supporting Information).

Light scattering measurement on **G5.0-PS-graft** and **G5.0-PS-graft-on-graft** gives $R_g/R_h = 1.3$ and 1.1, respectively. These lower values may indicate more condensed conformation than that of the precursor.

One purpose of the dendrimer-like dendrigrafts synthesis is to facilitate the AFM observation after densely grafting. The second generation dendrimer-like dendrigrafts (**G5.0-PS-graft-on-graft**) is visualized by AFM (Figure 16 and Figure S8, Supporting Information). The size of individual molecules increases from $\sim 45 \text{ nm}$ before grafting to $\sim 75 \text{ nm}$ after grafting; meanwhile, the height increases from 1.3 to 3.0 nm. The individual arms are visible due to the rigidity caused by densely grafted side chains. It is also clear that the central part is thicker than the periphery after collapse of the PS segments on mica. The properties of the functionalized dendrimer-like star polystyrene and copolymers with isoprene and MMA are currently under investigation.

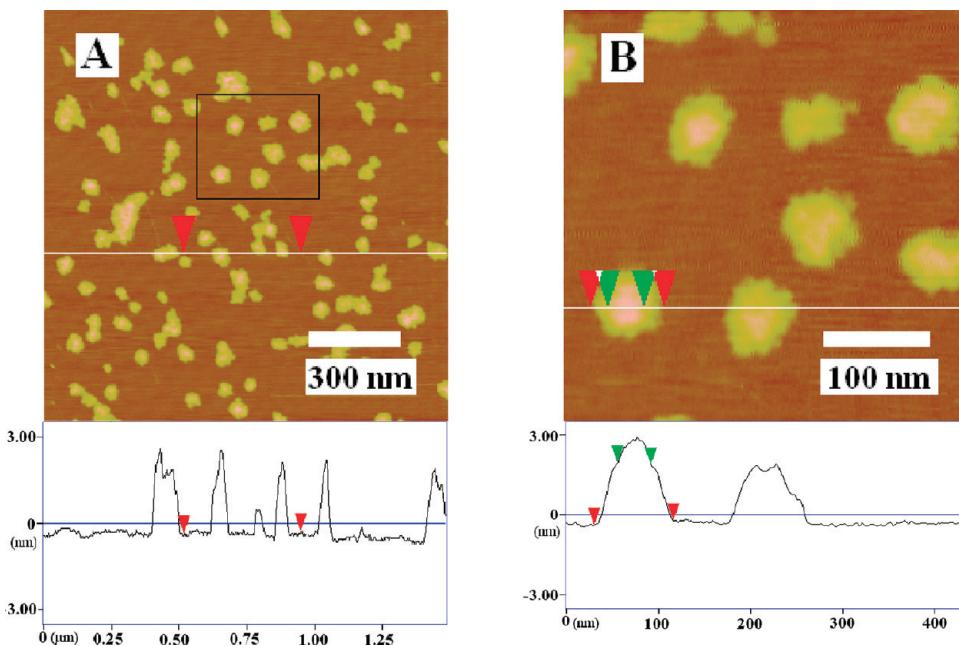


Figure 16. AFM images of G5.0-PS-graft-on-graft in a tapping mode by spin-coating on mica from CHCl₃ solution (0.05 mg/mL).

multiangle laser light scattering detector, He–Ne 658.0 nm), ViscoStar (Wyatt), and Optilab rEX (Wyatt). THF was used as the eluent at a flow rate of 1.0 mL/min at 35 °C. R_g was obtained by Zimm plot given by DAWN HELEOS in the off-line mode. dn/dc was determined in Optilab rEX in the off-line mode. AFM image was obtained in an instrument of NanoScope IV (Digital Instruments, Santa Barbara, CA) operated at tapping mode, using silicon tips of Model TESP (Digital Instruments) with radius of curvature of the tip less than 10 nm. Polymer solution (0.01–0.05 mg/mL) was spin-coated (1500 rpm for 5.0 s and then 2800 rpm for 1.0 min) on the surface of freshly cleaved mica. The MALDI–TOF mass spectrum was obtained from a Voyager DE-STR matrix-assisted laser desorption/ionization time-of-flight (MALDI–TOF) mass spectrometer equipped with a 337 nm nitrogen laser. A 10 μL sample solution (10 mg/mL in THF), 10 μL dithranol as the matrix (20 mg/mL in THF), and 2.0 μL silver trifluoroacetate (10 mg/mL in THF) were mixed, and then 0.50 μL of the mixed solution was dropped onto the plate and dried at ambient temperature. Mass spectra were given by a reflector mode using an acceleration voltage of 20 kV with an appropriate laser power and generally 1000 pulses were averaged. Transmission electron microscopy (TEM) images were recorded on a Tecnai G² 20 Twin TEM (FEI). The samples were prepared by placing one drop of CHCl₃ solution (0.01–0.05 mg/mL) on a copper grid coated with carbon. Before dynamic light scattering (DLS) measurements, all the sample solutions were filtered through 0.2 μm Millipore filters (Millipore Millex-FG, Phobic PTFE) to remove dust. The sample solutions were measured by an ALV-5000 Laser Light Scattering Spectrometer equipped with a multi- τ digital time correlation (ALV5000) and a He–Ne laser ($\lambda_0 = 632.8$ nm) light source at 30 °C and at a fixed scattering angle of 90°. The hydrodynamic radius (R_h) and polydispersity index (PDI) was obtained by the CONTIN program. R_g s of the samples were also determined on the ALV-5000. The sample solutions were carefully filtered through 0.2 μm Millipore filters (Millipore Millex-FG, Phobic PTFE) until there was not any dust found by DLS at 30°. After corrected by toluene and pure THF from 30° to 150° with a step of 5°, the static light scattering determination was performed on the same condition to give R_g . The dn/dc was obtained on Optilab rEX.

Preparation of Inimer and Difunctional Initiator. Glass apparatus were connected to the vacuum/argon line. The reactor with a magnetic stir bar inside was dried by five cycles of flaming/Ar-purging/evacuating. A volume of 6.0 mL cyclohexane solution of MDDPE (0.40 mmol/mL) was added, followed by distillation of cyclohexane to dryness. Then a volume of 70 mL of THF was distilled

into the flask, and the impurities was titrated by DPELi (adduct of s-BuLi and DPE) until red color appeared. THF was cooled to –80 °C by liquid nitrogen and acetone. s-BuLi (2 mL, 1.3 mmol/mL in cyclohexane) was slowly added and a dark red color appeared immediately. HPLC was used to trace the reaction until the MDDPE was consumed. The reaction proceeded for 15 min. THF was then completely distilled out and cyclohexane distilled into the flask at 0 °C. The inimer was obtained as stock solution in cyclohexane in volumetric ampules (the concentration of organolithium is ca. 0.08 mol/mL) and stored at 0 °C. The content of monoadduct in the final product is 96% as determined by GC–MS.

The preparation of diadduct is similar to that of monoadduct except two equivalent of s-BuLi is used. The resulting diadduct was stored at 0 °C in cyclohexane solution (the concentration of organolithium is ca. 0.04 mol/mL).

Model Reaction for the Branching Process. A solution of PSLi in cyclohexane, prepared by s-BuLi (1.0 mL, 1.3 M in cyclohexane) initiated polymerization of styrene (1.90 g, 18.3 mmol) at 45 °C, was mixed with a cyclohexane solution of inimer (30 mL, 4.33 × 10^{–2} mol/mL) in the presence of THF (double equivalent of Li). The reaction proceeded for 1.0 h and an aliquot of the react mixture containing the product, polystyryl α , α' -dianion, was analyzed using MALDI–TOF mass spectrometry. The resulting dianion was used *in situ* to initiate the polymerization of styrene to give a star-like PS ($M_{n,SEC} = 7800$ g/mol, PDI = 1.19, $M_{w,MALLS} = 9600$ g/mol).

Continuous Synthesis of Living Dendrimer-Like Star Polystyrenes. Glass apparatus were connected to the vacuum/argon line. The polymerization was carried out in a volumetric ampule with a magnetic stir bar inside which was dried by five cycles of flaming/Ar-purging/evacuating and rinsed sequentially with a dilute cyclohexane solution of *n*-BuLi and pure cyclohexane.

The preparation of dendrimer-like star polystyrene are described using the following reaction as an example. Cyclohexane (20 mL) was distilled into the reaction flask followed by adding 0.05 mL of THF as additive. A solution of diadduct of s-BuLi with MDDPE (as prepared above) (5.0 mL, 0.040 mmol/mL in cyclohexane), and styrene (1.72 g, 16.5 mmol, freshly distilled) were added to the flask at ~6 °C for 30 min, then raising the temperature to 45 °C for 60 min. After the polymerization, living G1.0-PS₄₃₀₀ was obtained and analyzed by SEC and NMR.

The living G1.0-PS₄₃₀₀ was mixed *in situ* with a solution of inimer (5.0 mL, 0.08 mmol/mL in cyclohexane). The addition reaction proceeded at 45 °C for 1.0 h to give living G1.5-PS₄₃₀₀. Half volume of

the reaction mixture was separated using a volumetric ampule, terminated with a solution of THF (20 mL) containing 1 mL of methanol and 0.10 mL of HCl (concentrated), and the intermediate product was precipitated into 300 mL of methanol. The residual reaction mixture was mixed with 15 mL dry cyclohexane containing 0.03 mL THF. Styrene (1.72 g, 16.5 mmol) was added to start the polymerization, followed by addition of inimer to the terminus of dendritic polymers. G2.5-PS₄₃₀₀ was obtained. Repeating the process gave dendritic products up to G5.5. TMEDA (\sim 0.03 mL) was used in the preparation of highest generation. The characterization results are listed in Table 1.

Functionalization of Living Dendrimer-Like Star Polystyrene with Allylic and Hydroxyl Groups. The living dendrimer-like star polystyrenes with various generations as prepared above were reacted with dry allyl bromide *in situ* in cyclohexane at 10 °C for 2 min. Dendrimer-like star polymers of G1.5-PS-vinyl to G5.5-PS-vinyl were obtained. The final product was fractionated from toluene/methanol with a yield of \sim 60%. ($M_{n,SEC}$ = 79.0×10^3 g/mol, PDI = 1.52, $M_{w,MALLS}$ = 255.0×10^3 g/mol).

The allyl group functionalized dendrimer-like star PS with 5.fifth generation (0.50 g), G5.5-PS-vinyl, was dissolved in toluene followed by adding 1-thioglycerol (2.0 mL) and a small amount of AIBN (6.0 mg, \sim 30% in mole ratio to allyl group). The oxygen was removed by freezing-thawing-evacuating for 3 times. The reaction was carried out at 80 °C for 6 h. The product was precipitated from methanol, and washed 2 times with methanol with the aid of centrifuge ($M_{n,SEC}$ = 85.0×10^3 g/mol, PDI = 1.62, $M_{w,MALLS}$ = 243.0×10^3 g/mol).

Synthesis of Living Dendrimer-Like Star Copolymers. Living G3.5-PS₃₃₀₀ ($M_{n,SEC}$ = 23.0×10^3 g/mol, PDI = 1.28, $M_{w,MALLS}$ = 45.0×10^3 g/mol) was used as a dendritic initiator to initiate the polymerization of isoprene (1.32 mL, 13.2 mmol). Upon addition of isoprene, the reaction solution changed from orange to pale yellow in color, indicating the initiation of isoprene. G4.0-PS-*b*-PI was obtained and fractional purification by toluene/methanol ($M_{n,SEC}$ = 30.2×10^3 g/mol, PDI = 1.52, $M_{w,MALLS}$ = 71.2×10^3 g/mol).

Living G3.5-PS₃₅₀₀ was used as a dendritic initiator for the polymerization of MMA. Thus, the reaction solution of G3.5-PS₃₅₀₀ was mixed with 50 mL of dry THF followed by feeding the MMA monomer at -78 °C. The polymerization proceeded for 1 h to give dendrimer-like star copolymers of G4.0-PS-*b*-PMMA ($M_{n,SEC}$ = 40.2×10^3 g/mol, PDI = 1.52, $M_{w,MALLS}$ = 96.8×10^3 g/mol).

Synthesis of G5.0-PS-Graft-on-Graft Polymers. Dendrimer-like star copolymer, G5.0-PS₂₇₀₀-*b*-PI (0.60 g, 0.0026 mmol), was dissolved in toluene and then mixed with 1 mL of HCOOH and 1.0 mL of H₂O₂ under stirring for 1.0 h at 35 °C. The reaction solution was washed by water two times. The product was precipitated in methanol and dried in vacuum for analysis. The epoxidized product was dissolved in THF followed by adding excessive presynthesized PI₁₀-*b*-PS₁₀Li in cyclohexane to accomplish the grafting reaction within 24 h at room temperature. The graft copolymer, G5.0-PS-graft, was obtained after precipitation in methanol and extraction by acetone to remove the excessive PS-*b*-PI arm polymers. The PI segments in G5.0-PS-graft were further epoxidized, and attacked by a presynthesized PSLi (M_n = 1100 g/mol) as arm. G5.0-PS-*graft-on-graft* was obtained. ($M_{n,SEC}$ = 484.0×10^3 g/mol, PDI = 1.21, $M_{w,MALLS}$ = 1.84×10^6 g/mol).

Titration of Vinyl Groups in Dendrimer-Like Star Polystyrenes Functionalized with Allylic Groups. The polymer of G5.5-PS₄₀₀₀-vinyl (0.4038 g, 0.00158 mmol) was dissolved in cyclohexane (10 mL) followed by adding excessive IBr in cyclohexane solution (4.00 mL, 0.1010 mmol/mL) to react with the vinyl groups for 3.0 h at room temperature. The residual IBr was reduced by KI (2.0 mL, 1.0 mmol/mL in water) to I₂ in 30 min. The mixture was titrated by sodium thiosulfate solution (22.0 mL, 0.029 mmol/mL) using starch aqueous solution as the indicator. Number of vinyl groups in the periphery was calculated by $N_{\text{vinyl, obs.}} = [N_{\text{IBr}} \cdot V_{\text{S}_2\text{O}_3^{2-}} \times [\text{S}_2\text{O}_3^{2-}]/2]/N_{\text{G5.0-PS-vinyl}}$.

Titration of Hydroxyl Groups in Functionalized Dendrimer-Like Star Polymer, G5.0-PS-OH. Dry sample of G5.0-PS-OH (0.3045 g, 1.19×10^{-3} mmol) was dissolved in THF (10 mL) which

was titrated by a DPELi in cyclohexane (2.83 mL, 0.0423 mmol/mL). The blank experiment was carried out in the absence of polymer under otherwise identical conditions. The number of hydroxyl groups in the periphery was estimated to be 92 ± 10 , according to the following equation:

$$N_{\text{hydroxyl groups, obs.}} = (V_{\text{DPELi}} \times [\text{DPELi}])/N_{\text{G5.0-PS-OH}}$$

in which V_{DPELi} is the consumed volume of DPELi at the concentration of [DPELi], and $N_{\text{G5.0-PS-OH}}$ represents a molar amount of polymer sample.

ASSOCIATED CONTENT

S Supporting Information

Results of SEC, ¹H NMR, and DLS, Tyndall phenomena, and AFM images of concerned dendrimer-like star (co)polymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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