Synthesis of Multi-Arm Star Polystyrene with Hyperbranched Polyester Initiators by Atom Transfer Radical Polymerization

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ABSTRACT: Multi-arm star polystyrenes with hyperbranched polyester (HP3) core were prepared by atom transfer radical polymerization (ATRP). The structures of the polymers were investigated with FTIR and ^{1}H NMR. GPC results showed that the resultant polymers had relatively broad polydispersity indices that arouse from the macromolecular initiator (HP3-Br). The thermal properties were studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC analysis indicated that polystyrene star polymers had only the glass transition temperatures (T_g), which changes with the weight ratio of multifunctional macroinitiator-to-monomer. In addition, these star polymers could form the spherical micelles in the selected solvent (THF/n-hexane). © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 728–733, 2006

Key words: multi-arm star polymers; hyperbranched polyester; atom transfer radical polymerization (ATRP); macroinitiator synthesis; self-assembly.

INTRODUCTION

The construction of polymer materials with controlled compositions, topologies, and functionalities has been the enduring focus in current research.[1–4] Among them, multi-arm star polymers have extensively been studied because of their substantial commercial potential as melt rheology modifier, compatibilizers for polymer blends, and emulsifiers.[5] In general, the two major synthetic routes that have been developed to prepare star shaped polymers are the "arm first,"[6] in which telechelic polymers are attached to a suitable core molecule in the final step of the reaction, and the "core first,"[7] in which a polyfunctional core is used as a multiple initiator for polymerization. So far, the core first method has proven very efficient to form regular stars, and a series of well-defined star polymers with precise arm numbers have been successfully synthesized by living radical polymerizations,[8–10] ring-opening polymerization (ROP),[11–13] group transfer polymerization,[14] and atom transfer radical polymerization (ATRP).[1,15,16] More recently, the combination of various polymerization techniques to prepare novel star polymers and star block copolymers has attracted much attention, since these combinatorial approaches can not only enrich the types of polymerizable monomers but also enable variable compositions, architectures, and properties into one polymeric structure. Especially, the synthesis of multi-arm hyperbranched polymers in the design of self-assembling systems by molecular recognition, self-replication, and self-organization based on noncovalent interactions has attracted increasing attention.[17] Some of the works demonstrated that multi-arm hyperbranched polymers with amphiphilic core-shell structure exhibited unimolecular reverse micelle properties, i.e., encapsulation and phase transfer of ionic guest molecules in analogy to amphiphilic dendrimers.[18,19] The intriguing self-assembly properties of multi-arm hyperbranched polymers have been explained by their hydrophobic shell/hydrophilic core structure, and they have potential applications as processing modifiers, toughening additives, drug delivery vehicles, synthesis supporting materials, advanced coatings, polymeric electrolytes, and optical wave guide materials.[20–22] Although significant progress has been made in the syntheses and applications of hyperbranched polymers, there is still very little detailed information on the self-assembly properties of such polymers.

In this contribution, we report on synthesis of novel multi-arm hyperbranched polyesters combination of self-condensing polymerization and ATRP, as shown in Scheme 1. It was found that self-assembled structures of novel hyperbranched
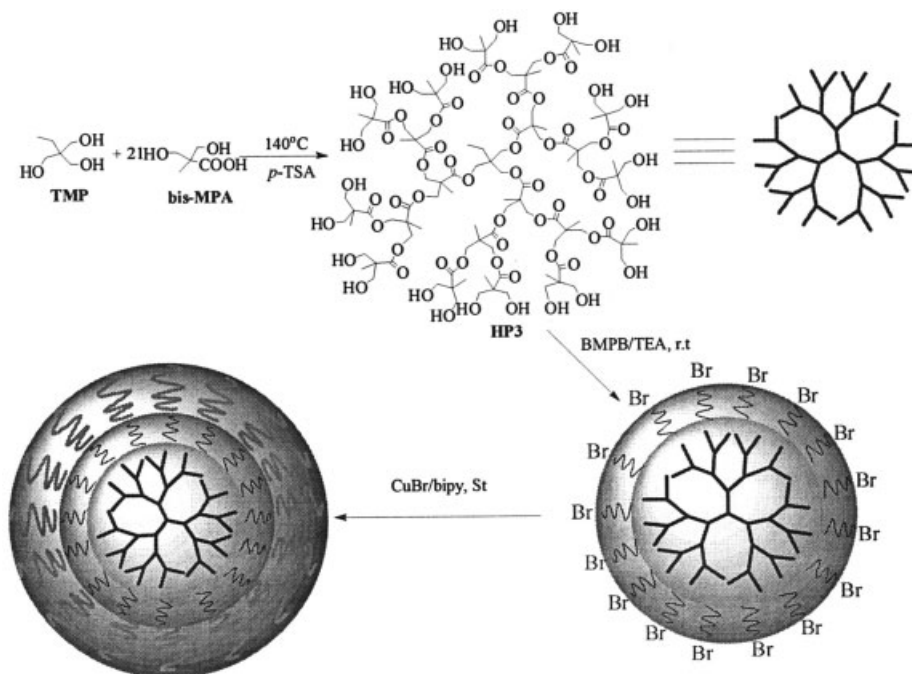
Scheme 1. Reaction scheme for synthesis of hyperbranched polyester and star-shaped hyperbranched polyester-cored polystyrene.

polyesters could be formed in selected solvents (THF/n-hexane).

EXPERIMENTAL

Materials

Chloroform (Reagent grade), acetone (Analysis grade), n-hexane (Analysis grade), dimethylformamide (DMF, Analysis grade), tetrahydrofuran (THF, Analysis grade) and triethylamine (TEA, Analysis grade), pyridine (Analysis grade), and 2,2′-bipyridyl (bipy, Analysis grade) were purchased from East of China Chem. Ltd. Co. and used as received. 2-Ethyl-2-hydroxymethyl-1,3-propanediol (TMP, 99%), 2,2-bis(hydroxymethyl) propionic acid (bis-MPA), p-toluene sulfonic acid (p-TSA), 2-bromo-2-methylpropionyl bromide (BMPB) were used as received from Across. Styrene (St) was distilled freshly before use.

Synthesis of hyperbranched polymers (HP3)

All synthetic procedures were made under a dry nitrogen atmosphere. Hyperbranched polyesters-polyol of a third generation with TMP as a core and bis-MPA was prepared by a procedure described in the literature.[23,24] Esterfication was carried out at 140°C with p-TSA as an acid catalyst. The chosen TMP: bis-MPA molar ratio of 1 : 21 corresponded to the theortical molecular weight of 2573 g/mol and a hyperbranched polyester with 24 terminal hydroxyl groups. The

crude polymer was precipitated from acetone in hexane and dried under vacuum. FTIR showed no remaining carboxylic acid. ^{1}H NMR (δ, ppm): 1.0–1.3 (—CH_3), 2.0–2.1 (—CH_2OH), 3.6–3.7 (—CH_2OH), 4.10–4.32 (—COOCH_2—).

Synthesis of hyperbranched polyester initiators (HP3-Br)

All operations were carried out under nitrogen atmosphere. A sample of HP3 was placed in 50.0 mL of anhydrous DMF, and 0.5 mL of pyridine and 3.0 mL of TEA were added. Then, 5.0 mL of BMPB was added dropwise at 0°C for 10 min. The mixture was stirred for 1 h at 0°C followed by stirring at room temperature for another 24 h. Then, the solid was separated from the mixture by filtration and then washed with 100 mL acetone. ^{1}H NMR (δ, ppm): 1.0–1.3 (—CH_3), 1.91–1.92 (—C(CH_3)$_2$Br), 2.0–2.1 (—CH_2OH), 3.6–3.7 (—CH_2OH), 4.10–4.32 (—COOCH_2—).

Synthesis of multi-arm star copolymer (HP3-PS)

The multi-arm star copolymers were synthesized in the presence of the hyperbranched polyester macroinitiator (HP3-Br) in toluene with Cu(I)Br as catalyst and bidy as ligand. Typically, an oven-dried Schlenk tube was charged with HP3-Br multi-arm macroinitiator, Cu(I)Br, toluene, and a magnetic stirrer, and degrassed for three cycles by pulling vacuum and back-

filling with nitrogen gas. Then, styrene was added via syringe. The reaction was carried out at 90°C for 12 h, and then cooled to room temperature. The sample was further diluted with $CHCl_3$, removed copper salts through a plugged column of neutral aluminum oxide, and precipitated in a large volume of acetone. The sample was purified by reprecipitating three times from $CHCl_3$ to n-hexane and dried in a vacuum oven overnight at 50°C. The conversion of polymerization was determined gravimetrically. ^{1}H NMR (δ, ppm): 1.04–1.30 (—CH_3), 1.25–2.40 (—CH_2OH for HP3 moniety, —CH_2— and >CH— for PSt moniety), 3.6–3.7 (—CH_2OH), 4.10–4.32 (—COOCH_2—), 6.39–6.84 and 6.97–7.36 (—PhH for PS).

Characterization

^{1}H NMR spectra were recorded with an AVANCE DMX-500 NMR spectrometer by using tetramethylsilane (TMS) as internal standard at room temperature. The gel permeation chromatography (GPC) measurements were carried out on a Waters 201 with a μ-styragel column and THF or DMF as an eluent, and the molecular weight was calibrated with standard polystyrene (PS). Differential scanning calorimetry (DSC) was carried out on a DS822, with a heating rate of 10°C/min from 30 to 200°C under nitrogen atmosphere, relative to indium standards. Infrared spectra were recorded on Jasco IR-700 infrared spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Netzsch STA 409 PG/PC instrument (Germany) at a heating rate of 20°C/min from 40 to 500°C in a flow of nitrogen. Transmission electron micrographs were obtained on a JEOL model 1200EX instrument operated at an accelerating voltage of 160 kV.
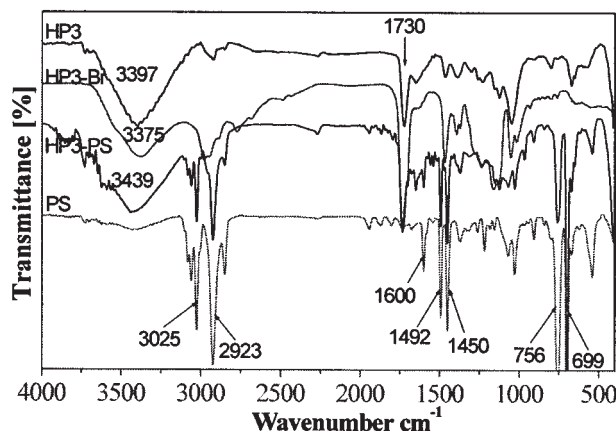
RESULTS AND DISCUSSION

Synthesis and characterization of HP3-PS

The HP3-Br was synthesized by the reaction of polyester (HP3) and BMPB at 0°C in the presence of TFA
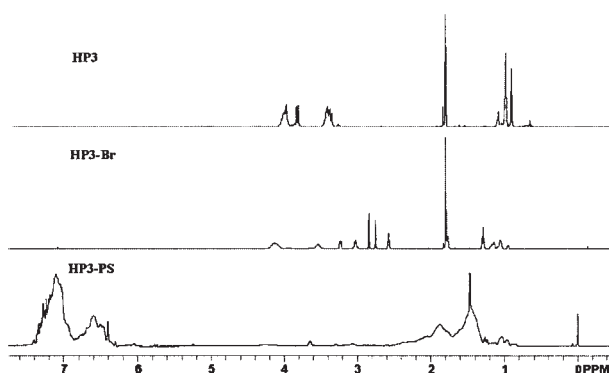
Figure 1 ^{1}H NMR spectra of hyperbranched polyester (HP3), macroinitiator, and multi-arm hyperbranched star polystyrene (HP3-PS$_3$).

Figure 2 FTIR spectra of hyperbranched polyester (HP3), macroinitiator (HP3-Br), multi-arm hyperbranched star polystyrene (HP3-PS$_3$), and ordinary polystyrene (PS1).

and pyridine in DMF as solvent. When HP3-Br is the initiator and CuBr/2,2'-bipyridyl is the catalyst, then the polymerization of styrene occurs by atom transfer radical polymerization (ATRP) to yield multi-arm star copolymers. A large number of initiating centers on the same molecules greatly increase the possibility of crosslinking by coupling side reactions of the numerous growing radical chain-ends. In our case, the core hyperbranched polymer HP3-Br with an average of 7.5 initiating sites per molecule was used to initiate the polymerization, and no insoluble crosslinked materials were found. However, it is estimated that the coupling reactions of the growing radical chain-ends could still exist to some extent to form the soluble coupling products.[25]

Its characterization was investigated with ^{1}H NMR and FTIR. As can be seen in Figure 1, there are new signals at 1.92 ppm from [—C(CH$_3$)$_2$Br] ^{1}H NMR spectrum, which is not present in the hyperbranched polyester (HP3). Therefore, the HP3-Br was successfully synthesized. The characteristic absorption peak of the polyester at 1730 cm^{-1}, which is also present in the macroinitiator (HP3-Br), is contributed to the C=O stretching vibration. However, the variation of the peak intensity increases after substitution by the BMPB (Fig. 2). It is known that the tertiary bromoester- groups are effective initiator for ATRP of methylacrylate and styrene derivatives.[26] The multifunctional macroinitiator was used to initiate the monomer styrene (St) for the multi-arm star copolymer by ATRP.

To obtain different degrees of polymerization, the ratio of monomer-to-initiator was varied (Table I). From Figure 1 we can observe the characteristic resonance originating from phenyl moieties at both 6.39–6.84 and 6.97–7.36 ppm in HP3-PS. In the FTIR spectrum of HP3-PS, the characteristic stretching vibration of HP3-Br at 1730 cm^{-1} (C=O) and ordinary PS at

TABLE I
Characteristics of Multi-Arm Star Hyperbranched Polystyrene

Compound[a]	GPC[b]			Yield (%)[c]	T_g(°C)
	M_n (10^4 g/mol)	M_w (10^4 g/mol)	M_w/M_n		
HP3	0.16	0.22	1.40	95.0	34.0
HP3-Br	0.27	0.36	1.35	89.2	—
PS1	20.51	4.07	1.98	92.0	100.5
HP3-PS$_1$	2.55	3.57	1.40	50.3	87.2
HP3-PS$_2$	1.84	2.62	1.42	45.6	64.7
HP3-PS$_3$	0.95	1.27	1.34	37.2	42.7
PS2	15.51	30.31	1.95	90.0	97.5
HP3-PS$_4$	3.09	4.66	1.51	51.5	92.7
HP3-PS$_5$	2.03	2.94	1.45	47.3	72.5
HP3-PS$_6$	1.02	1.53	1.49	35.6	52.5
PS3	11.79	24.74	2.09	90.0	98.2
HP3-PS$_7$	3.17	4.69	1.48	52.3	97.2
HP3-PS$_8$	2.15	3.14	1.46	45.3	72.7
HP3-PS$_9$	0.95	1.40	1.47	25.6	49.7

[a] Homopolymer (PS$_n$) was synthesized at 100 ($n = 1$), 110 ($n = 2$), and 120°C ($n = 3$) without initiator, ligand, and catalyst. Copolymer (HP3-PS$_n$) was synthesized by ATRP, using HP3-Br as initiator, bipy as ligand, and Cu(1)Br as catalyst. Polymerization time is 12 h; polymerization temperature is 100°C ($n = 1–3$), 110°C ($n = 4–6$), and 120°C ($n = 7–9$); molar ratio of monomer (St), macroinitiator (HP3-Br), ligand (bipy), and Cu(I)Br is 450 : 1 : 1 : 2 ($n = 1, 4,$ and 7), 350 : 1 : 1 : 2 ($n = 2, 5,$ and 8), 150 : 1 : 1 : 2 ($n = 3, 6,$ and 9).
[b] As calibrated against linear polystyrene stands with low polydispersity index. The eluent for samples was THF, except HP3 and HP3-Br using MDF.
[c] Yield% = $[W_{HP3-PSn}/(W_{St} + W_{HP3-Br})] \times 100\%$, where $W_{HP3-PSn}$, W_{St}, and W_{HP3-Br} are the weights of the multi-arm hyperbranched polystyrene, monomer (St), and macroinitiator (HP3-Br).

3025 cm^{-1}, C—H stretching vibration on phenyl and methylene moieties at 2923 cm^{-1}, and C—C curving vibration on phenyl and methylene segments at 1492 cm^{-1}, 1450 cm^{-1} and 756 cm^{-1}, 699 cm^{-1} are all consisted in HP3-Br, which indicates that multi-arm star polystyrene was successfully obtained.

Figure 3 depicts GPC curves of some multi-arm star polymers. From GPC analysis, the polydispersity of multi-arm star copolymer was around 1.50. The GPC peak of the multi-arm star polymers shifted towards higher molecular weight with increasing the content of monomer in the reaction system. However, the molecular weight of multi-arm star polymers is much lower than that of PS obtained at the same temperature. Also, there is only one peak in the GPC curves, which rules out the formation of homo-polystyrene or other side polymerization.[27] So far, the hyperbranched macroinitiator HP3-Br can initiate St to produce the multi-arm star PS by ATRP.
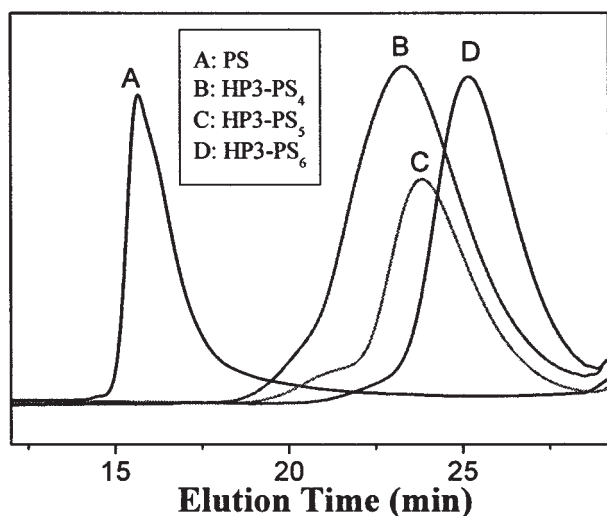

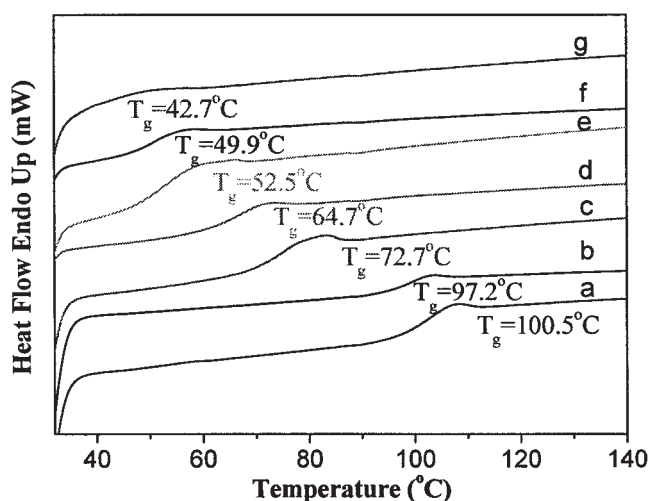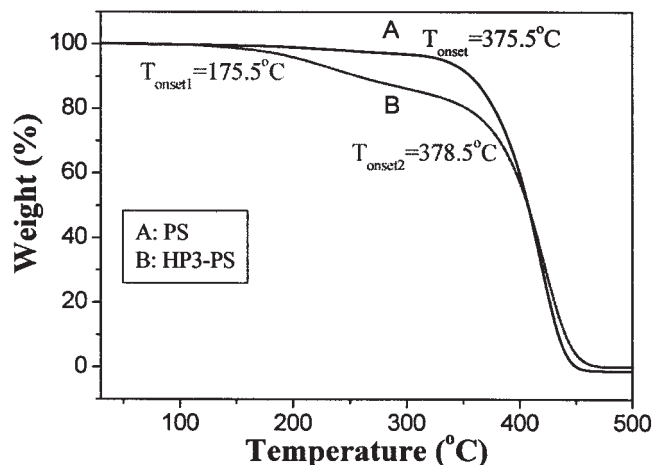**Figure 3** GPC spectra of homopolymer polystyrene (PS2) and some hyperbranched star polystyrene (HP3-PS_n, $n = 4$ –6).

Figure 4 DSC curves of homo-polystyrene and multi-arm star PS with polyether core (a: PS1; b: HP3-PS$_7$; c: HP3-PS$_8$; d: HP3-PS$_2$; e: HP3-PS$_6$; f: HP3-PS$_9$; g: HP3-PS$_3$).

Figure 5 TGA curves of homo-polystyrene and multi-arm star PS HP3-PS$_7$ (A: PS3 and B: HP3-PS$_5$).

Thermal properties of HP3-PS

Figure 4 presents the second heating DSC curves of the multi-arm star copolymers. To investigate the glass transfer temperature (T_g) of the multi-arm star copolymers, the different weight ratio of multi-functional macroinitiator-to-monomer was varied to control the degree of polymerization of each arm. From Figure 4 and Table I, T_g of the multi-arm star copolymers increases gradually with the content of PS in copolymers or molecular weight of copolymers. Meanwhile, glass transition temperature (T_g) observed throughout the whole scan ranged from 30 to 140°C. It was possible that the hyperbranched polyester core was compatible with the PS arms.

By way of TGA, we gain the curves of the loss weight rate of homo-polystyrene and multi-arm star PS in a nitrogen stream from room temperature to 500°C. Figure 5 gives the results of the PS3 and HP3-PS$_7$. It is found that the thermal stability of the two types of polymers is clearly different. As indicated in Figure 5, the initial decomposition temperature (T_{onset}) of homo-polystyrene is 375.5°C. However, in the case

of HP3-PS$_7$, two decomposition temperatures are observed: the first decomposition temperature (T_{onset1}) is 175.5°C, and the loss is about 15% up to 340°C, which contributes to the decomposition of hyperbranched polyester cores. The second decomposition temperature (T_{onset2}) is 378.5°C, which is near the initial decomposition temperature (T_{onset}) of the homo-polystyrene. The decompositions of the two polymers are almost absolute at 450°C.

Self-assembly properties of HP3-PS

Different morphologies of self-assembly systems are basically related to the chemical composition of the copolymer and to the relative volume ratio of the two blocks. Among the possible morphologies, spherical micelles are of special interest because they have the lowest of the surface energies[28] and can lead to encapsulating active molecules, such as DNA, enzymes, or drugs. Figure 6 shows micrographs obtained from a solution of the multi-arm star PS in THF/n-hexane (1:1 v/v) with concentration at 5 mg/mL. The spherical micelles with diameter around 120 nm are observed.

Different morphologies of self-assembly systems are basically related to the chemical composition of the copolymers. The multi-arm hyperbranched polymers (HP3-PS) consist of two segments: a hyperbranched polyester core and many PS arms, because both the core and the arms can be dissolving in trichloromethane. However, n-hexane is a good precipitator for hyperbranched core. Therefore, it is assumed that the excess PS arms are encapsulated in the aggregates and HP3 cores are hidden in the center of the micelles.

CONCLUSIONS

Novel multi-arm star hyperbranched polyester-cored polystyrenes with different molecular weight were synthesized successfully by ATRP, using HP3-Br in the presence of Cu(I)Br and bidy as catalyst system. The structures of polymers were confirmed by FTIR
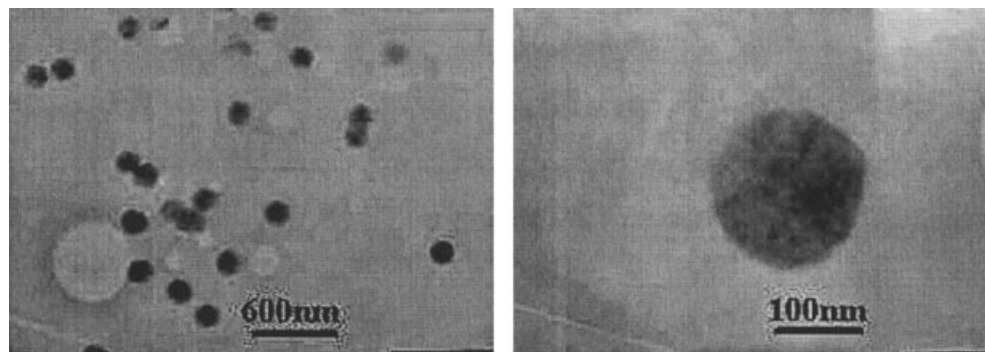
Figure 6 TEM images of HP3-PS1 obtained from tetrahydrofuran/n-hexane (1 : 1 v/v) with a concentration of 5 mg/mL.

and ^{1}H NMR. GPC results showed that the resultant polymers had relatively broad polydispersity indices that arouse from the macromolecular initiator (HP3-Br). DSC analysis indicated that PS star polymers had only the glass transition temperatures (T_g), which changes with the weight ratio of multi-functional macroinitiator-to-monomer. In addition, these star polymers could form the spherical micelles in the selected solvent (THF/n-hexane).

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