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Synthesis of multi-arm star polystyrene with hyperbranched polyether core

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Abstract

Multi-arm star polystyrenes with hyperbranched poly(3-ethyl-3-oxetanemethanol) (PEOM, **3**) core were synthesized by atom transfer radical polymerization (ATRP) method. The structures of polymers were confirmed by FT-IR and ^{1}H NMR. GPC results showed that the resultant polymers had relatively low polydispersity indices (PD = 1.47–2.03). DSC analysis indicated that polystyrene star polymers had a glass transition temperature (T_g = 42.2–91.5 °C) that changed with the amount of the polystyrene in the polymers. In addition, the aggregation behavior of the multi-arm star polystyrenes in a selective solvent (THF/cyclohexane) was probed with polystyrene arms that encapsulated in the aggregates and PEOM cores hidden in the center of the micelles.

Keywords: Multi-arm star polymers; Hyperbranched polyether; Atom transfer radical polymerization (ATRP); Macroinitiator; Synthesis; Self-assembly

1. Introduction

The construction of polymer materials with controlled compositions, topologies, and functionalities has been the enduring focus in current research [1–4]. Among of them, multi-arm star polymers have extensively studied due to a substantial commercial potential as melt rheology modifier, compatibilizers for polymer blends and emulsifiers [5–7]. In general, there are the two major synthetic routes that have been developed to prepare star shaped polymers are the 'arm first' [8], i.e., telechelic polymers are attached to a suitable core molecule in the final step of the reaction, and the 'core first' [9], i.e., 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 [10–12], ring-opening polymerization (ROP) [13–16], group transfer

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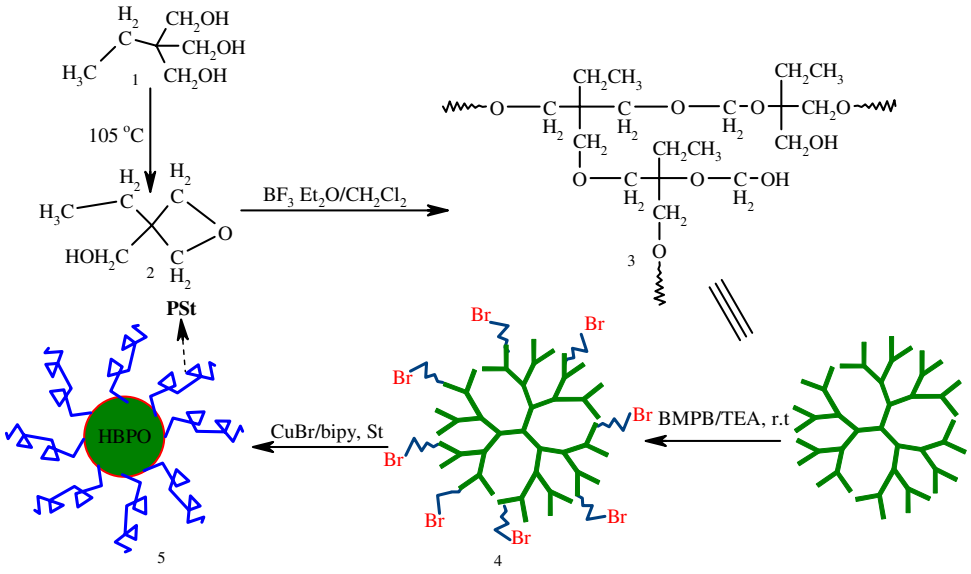

Scheme 1. Reaction scheme for synthesis of hyperbranched polyether and star-shaped hyperbranched polyether-cored polystyrene.

polymerization [17] and atom transfer radical polymerization (ATRP) [1,18,19].

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 [20–26]. Such aggregation has been attributed to intermolecular interactions between the non- or less-solvated blocks which are components in linear amphiphilic diblock or triblock copolymers. In polymer associations, however, that the extent to which intramolecular attraction also participates and contributes to the process of forming micelles and vesicles constructed by intermolecular aggregates, is not negligible. Good candidates to meet such inter and intramolecular interactions could be multi-arm star amphiphilic block copolymers, the presence of several identical blocks tied to a star core enables the stars to aggregate with both intramolecularly and intermolecularly resulting in shaped objects [27,28].

In this contribution, a multi-functional macroinitiator for ATRP has been synthesized by reacting a hyperbranched polyether, based on 3-ethyl-3-(hydroxymethyl)oxetane, with 2-bromo-isobutylbromide. It was used for the ATRP of styrene, as shown in Scheme 1. This yielded a co-polymer with a multi-arm star architecture. Furthermore, it was found that self-assembled nanostructures of the polystyrene could be formed in the selected solvents (THF/cyclohexane).

2. Experimental section

2.1. Materials

Chloroform (Reagent grade), acetone (Analysis grade), cyclohexane (Analysis grade), demethylformamide (DMF, Analysis grade), tetrahydrofuran (THF, Analysis grade) and triethylamine (TEA, Analysis grade), diethyl carbonate ($(C_2H_5O)_2CO$, Analysis grade), potassium hydroxide(KOH, Analysis grade) cuprous bromide (CuBr, Analysis grade) and 2,2′-bipyridyl (bipy, Analysis grade) were purchased from East of China Chem. Ltd. Co., and used as received. Boron trifluoride etherate ($BF_3 \cdot OEt_2$, Analysis grade) was dried by 4A molecular sieves and styrene (St, Analysis grade) was distilled freshly before used. Trimethyloxypropane (TMP, 99%) and 2-bromo-2-methylpropionyl bromide (BMPB) were used as received from Acros.

2.2. Synthesis of 3-ethyl-3-(hydroxymethyl)oxetane (2)

3-Ethyl-3-(hydroxymethyl)oxetane (**2**) was prepared by a modified procedure described in the literature [29]. A mixture of trimethyloxypropane (**1**, 26.8 g, 0.2 mol), diethyl carbonate (23.6 g, 0.2 mol),

potassium hydroxide (0.1 g, 1.8 mmol) in 2 ml of absolute ethyl alcohol was refluxed in oil bath at 110 °C for 1 h. Then, the mixture was distilled at 110 °C for 1 h. Distillation was continued until the oil bath was 140 °C. After the distillation, the vacuum was supplied for 1 h to remove the excess solvent. Upon heating above 185 °C, the distilled materials were collected in the cold trap under vacuum and obtained with more than 85% of the theoretical yield. ^{1}H NMR (δ, ppm): 0.80–0.83 (t, 3H, –CH_2CH_3), 1.61–1.66 (q, 2H, –CH_2CH_3), 3.62 (s, 2H, –CH_2OH), 3.66 (s, 1H, –CH_2O*H*), 4.31–4.32 and 4.38–4.39 (d, 4H, –CH_2O).

2.3. Cationic ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (**2**) using $BF_3 \cdot OEt_2$ [30–32]

The cationic polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (**2**) directly initiated by $BF_3 \cdot OEt_2$, polymerization was carried out at under a dry nitrogen atmosphere in a three-necked round-bottomed flask with a stirrer and a funnel. The reaction temperature was controlled at 0 °C and after 24 h the polymerization was quenched with water. The poly(3-ethyl-3-oxetanemethanol) (PEOM, **3**) was precipitated in distilled water and dried at 100 °C under vacuum. ^{1}H NMR (δ, ppm): 0.82–0.85 (–CH_3), 1.16–1.29 (–CH_2CH_3), 2.85–3.10 (–OCH_2–), 3.35–3.68 (–CH_2OH).

2.4. Synthesis of hyperbranched polyether initiators (4, PEOM-Br)

All operations were carried out under nitrogen atmosphere. A sample of PEOM was placed in 50.0 ml of anhydrous DMF. 0.5 ml of pyridine and 3.0 ml of triethylamine were added. Then 5.0 ml of 2-bromo-2-methylpropionyl bromide (BMPB) was dropwise at 0 °C in 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_2O*H*), 3.6–3.7 (–CH_2OH), 4.10–4.32 (–COOCH_2–).

2.5. Synthesis of multi-arm star copolymer (5, PEOM-PSt)

The multi-arm star copolymers were synthesized in the presence of the hyperbranched polyether macroinitiator, PEOM-Br, in toluene with Cu(I)Br as catalyst and bipy as ligand. Typically, an oven-dried Schlenk tubes was charged with hyperbranched polyether initiators (PEOM-Br), Cu(I)Br, toluene and a magnetic stirrer, and degrassed three cycles by pulling a 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 cyclohexane 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_2O*H* for PEOM moniety, –CH_2– and >C*H*– for PSt moniety), 6.39–6.84 and 6.97–7.36 (–Ph*H* for PS).

2.6. 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 performed at 40 °C on a Waters 201 with tetrahydronfuran (THF) or dimethylformamide (DMF) as an eluent at a flow rate of 1 ml/min. The samples were separated through four 5-μm PL gel columns. The relative molecular weights were calculated against 19 polystyrene standards. 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 by using films for liquids and KBr pellets for solids. 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 at 160 kV.

3. Results and discussion

3.1. Synthesis and characterization of PEOM-PSt

The synthetic procedure for hyperbranched polymers is outlined in Scheme 1. Aliphatic hyperbranched polymer with multi-functional hydroxy

groups was firstly synthesized by the cationic polymerization of 3-ethyl-3-(hydroxymethyl)oxetane (**2**) directly initiated by $BF_3 \cdot OEt_2$ [30]. Then, the hyperbranched polyether macroinitiator (PEOM-Br) was synthesized by reacting the polyether (PEOM) and 2-bromo-2-methylpropionyl bromide. Using hyperbranched polyether macroinitiator (PEOM-Br) as the initiator and Cu(I)Br/bipy as the catalyst, 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 PEOM-Br with an average of 8.3 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 [30].

The characterization of multi-arm star polymers were investigated with ^{1}H NMR and FT-IR. As shown in Fig. 1, the characteristic absorption peak of the hyperbranched polyether (PEOM) about at 3300 cm^{-1}, that is contributed to the O–H stretching vibration. After the hydrogen groups of PEOM partly substituted by the 2-bromo-2-methylpropionyl bromide, a characteristic absorption peak at 1730 cm^{-1} which belonged to the C=O stretching vibration is appeared. It is known that the tertiary bromoester-groups are effective initiator for ATRP of methylacrylate and styrene derivatives [33]. In the case of multi-arm star polystyrene (PEOM-PS), these characteristic absorption peaks are hard to observe

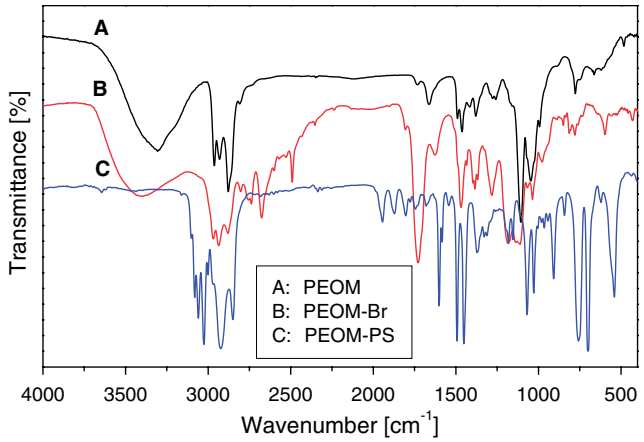

Fig. 1. FT-IR spectra of hyperbranched polyether (PEOM), hyperbranched polyether initiator (PEOM-Br) and multi-arm star polystyrene (PEOM-PS_1).

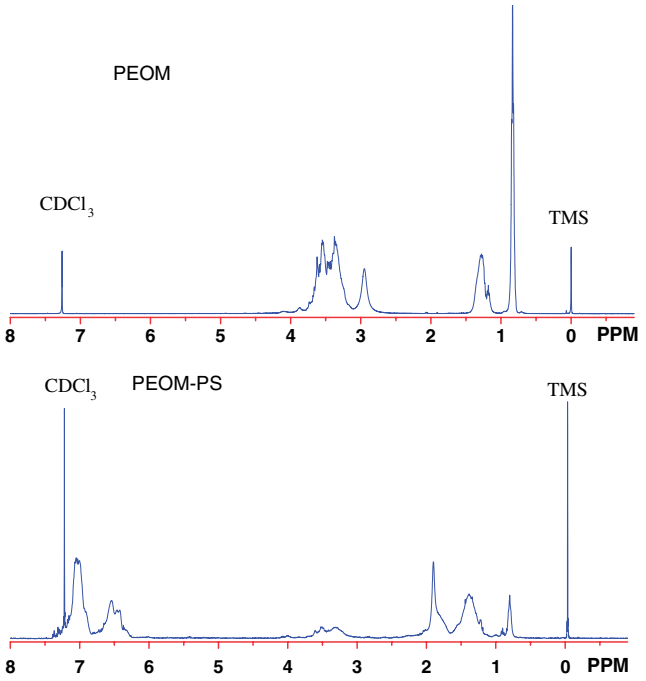

Fig. 2. ^{1}H NMR spectra of hyperbranched polyether (PEOM) and multi-arm star polystyrene (PEOM-PS_7).

for enwrapping a thick of polystyrene outside of hyperbranched polymer core. The similar conductions are also observed in the ^{1}H NMR (Fig. 2).

In order to obtain different degrees of polymerization, the reaction temperature and ratio of monomer-to-initiator was varied. As shown in Table 1, the M_n (or M_w) of multi-arm star PSt increases as improving the reaction temperature or ratio of monomer-to-initiator. Fig. 3 depicts GPC curves of some multi-arm star polymers. From GPC analysis, the

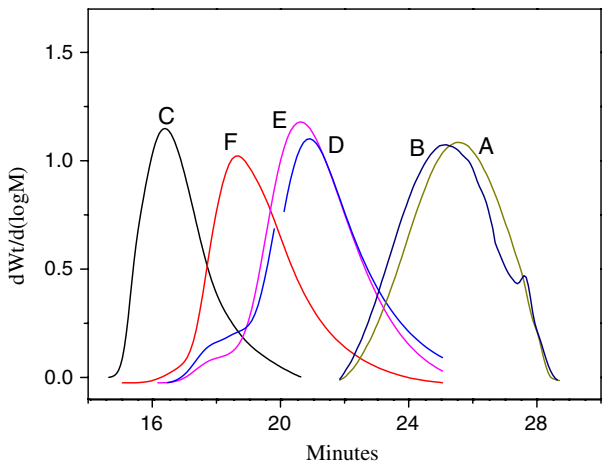

Fig. 3. GPC spectra of hyperbranched polyether (A: PEOM), Hyperbranched polyether initiator (B: PEOM-Br), homopolymer polystyrene (C: PS_2) and some multi-arm star polystyrene (PEOM-PS_n, D: 4, E: 5, F: 6).

Table 1
Characteristics of multi-arm star polystyrene

Compound[a]	GPC[b]			Yield (%)[c]	PD[d]	T_g (°C)
	M_n ($\times 10^{-4}$ g/mol)	M_w ($\times 10^{-4}$ g/mol)	M_w/M_n			
PEOM	0.15	0.24	1.61	95.0	–	34.0
PEOM-Br	0.28	0.43	1.56	89.2	–	–
PS_1	12.27	21.44	1.75	92.0	–	105.6
PEOM-PS_1	1.41	2.48	1.75	45.6	13.1	76.1
PEOM-PS_2	1.11	2.26	2.03	50.3	9.6	58.9
PEOM-PS_3	0.74	1.14	1.54	37.2	5.4	42.2
PS_2	15.48	28.49	1.84	90.0	–	106.7
PEOM-PS_4	1.95	2.97	1.53	47.3	19.4	77.2
PEOM-PS_5	1.37	2.19	1.59	51.5	12.7	73.9
PEOM-PS_6	0.78	1.55	1.98	35.6	5.8	50.4
PS_3	28.44	43.34	1.52	90.0	–	106.9
PEOM-PS_7	3.11	5.13	1.65	52.3	32.8	91.5
PEOM-PS_8	1.55	2.28	1.47	45.3	14.7	88.5
PEOM-PS_9	1.25	1.85	1.48	25.6	11.3	56.9

[a] Homopolymer (PS_n) was synthesized at 100 °C ($n = 1$), 110 °C ($n = 2$) and 120 °C ($n = 3$) without initiator, ligand and catalyst. Copolymer (PEOM-PS_n) was synthesized by ATRP using PEOM-Br as initiator, bipy as ligand and Cu(I)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 (PEOM-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 or DMF (PEOM and PEOM-Br).

[c] Yield (%) = $[W_{\text{PEOM-PS}n}/(W_{\text{St}} + W_{\text{PEOM-Br}})] \times 100\%$, where $W_{\text{PEOM-PS}n}$, W_{St} and $W_{\text{PEOM-Br}}$ are the weights of the multi-arm hyperbranched polystyrene, monomer (St) and macroinitiator (PEOM-Br).

[d] PD (average degree of polymerization of polystyrene) = $[M_n$ (PEOM-PS_n) − M_n (PEOM-Br)]/[8.3 × M (St)], where 8.3 is the average initiating sites per molecule.

polydispersity of multi-arm star copolymer was around 1.50. The GPC peak of the multi-arm star polymers shifted toward 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 polystyrene obtained at the same temperature. So far, the hyperbranched macroinitiator PEOM-Br can initiate St to produce the multi-arm star polystyrene by ATRP.

3.2. Thermal properties of PEOM-PSt

By way of TGA, we gain the curves of the loss weight rate of hyperbranched polyether and multi-arm star polystyrene in a nitrogen stream from room temperature to 550 °C. Fig. 4 gives the results of the PEOM and PEOM-PS_n ($n = 4 \sim 6$). It is found that the thermal stability of the two types of polymers is clearly difference. As indicated in Fig. 4, in the case of PEOM, the first weight lose is about 25% from heating (r.t.) to 150 °C and decomposition almost complete at 400 °C. However, in the cases of PEOM-PS polymers, two decomposition temperatures are observed, the first decomposition temperature (T_{onset1}) is 110 °C, and lose about 10–15% up to 250 °C, which contributing to the decomposition of hyperbranched polyether (PEOM) cores. These are consistent with the GPC results. The second decomposition temperature (T_{onset2}) is 370 °C which is near the initial decomposition temperature (T_{onset}) of homo-polystyrene. The decompositions of multi-arm star polymers are almost complete at 450 °C.

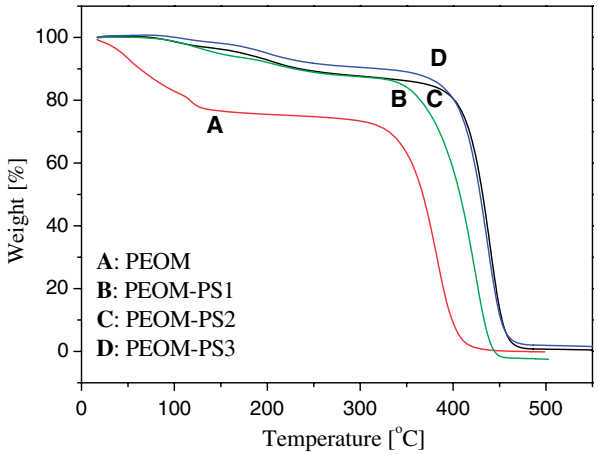

Fig. 4. TGA curves of hyperbranched polyether (PEOM) and (PEOM-PS_1, PEOM-PS_2 and PEOM-PS_3).

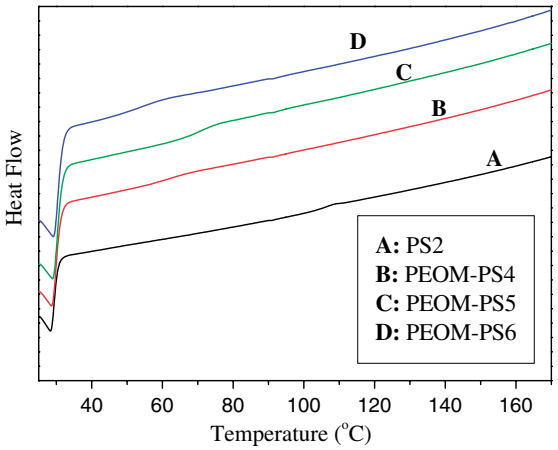

Fig. 5. DSC curves of polystyrene (PS_2) and multi-arm star polystyrene (PEOM-PS_4, PEOM-PS_5 and PEOM-PS_6).

Fig. 5 presents the second heating DSC curves of the multi-arm star copolymers. To investigate the glass transfer temperature (T_g) of the homo-polystyrene and 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 Fig. 5 and Table 1, T_g of the multi-arm star copolymers increase gradually with the content of polystyrene in copolymers or molecular weight of copolymers. Meanwhile, the only glass transition temperature (T_g) observed throughout the whole scan range from 30 to 140 °C. It was possible that the hyperbranched polyether core was compatible with the polystyrene arms.

3.3. Self-assembly properties of PEOM-PSt

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 [34–36,9] and can lead to encapsulating active molecules such as DNA, enzymes, or drugs.

Fig. 6A shows micrographs obtained from a solution of the multi-arm star polystyrene in THF/cyclohexane (1:1, v/v) with concentration at 5 mg/ml. The spherical nanoparticles with diameter around 100–350 nm are observed. From the magnification TEM image, many grainy objects are observed on the surface of the micelles (inset in Fig. 6A). It is well known the different morphologies of self-assembly systems are basically related to the chemical composition of the copolymers. The multi-arm hyperbranched polymers (PEOM-PS) consist of two segments: a hyperbranched polyether core and many polystyrene (PS) arms. Because both of core and arms can be dissolving in THF, however, cyclohexane is a poor solvent for hyperbranched core. Therefore, it is assumed that the excess polystyrene arms are encapsulated in the aggregates and PEOM cores are hidden in the center of the nanoparticles (Fig. 6B).

4. Conclusions

Novel multi-arm star hyperbranched polyether-cored polystyrene with different molecular weight were synthesized successfully by ATRP using hyperbranched polyether macroinitiator in the presence of Cu(I)Br and bipy as catalyst system. The structures of polymers were confirmed by FT-IR and ^1H NMR. GPC results showed that the resultant polymers had low polydispersity indices (PD = 1.47–2.03). DSC analysis indicated that polystyrene star polymers had only glass transition temperatures (T_g = 42.2–91.5 °C) that varied with the content of polystyrene in multi-arm star polystyrene. In addi-

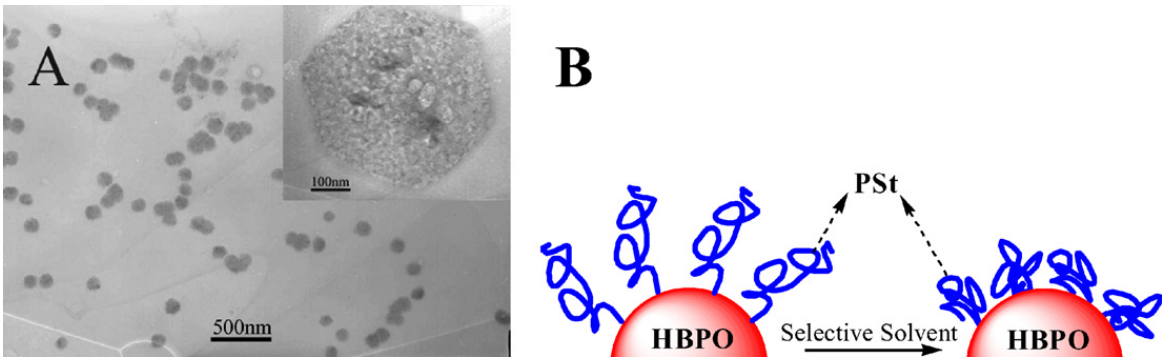

Fig. 6. TEM images of PEOM-PS_1 obtained from tetrahydrofuran/cyclohexane (1:1, v/v) with concentration at 5 mg/ml (A) and self-assembly procedure of multi-arm star polystrene (PEOM-PSt) (B).

tion, self-assembly nanoparticles of the multi-arm star polystyrene could be found in the selected solvent (THF/cyclohexane).

Acknowledgement

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