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Effect of Degree of Branching on the Self-Assembly of Amphiphilic Hyperbranched Multiarm Copolymers

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Introduction

Being regarded as a significant kind of functional polymer, hyperbranched polymers (HBPs) are highly branched macromolecules with 3D dendritic globular architecture, which have the advantages of facile one-pot fabrication, a large population of terminal functional groups, lower viscosity, and better solubility.[1,2] For HBPs, the degree of branching (DB) is one of the most important intrinsic parameters, which gives birth to great influence on the physical and chemical properties of polymer materials.[3−9]

In the last two decades, molecular self-assembly of linear block copolymers has demonstrated great potential in the preparation of highly ordered and functional structures on all scales.[10−18] As an extension of macromolecular self-assembly, very recently, HBPs have displayed great potential as excellent precursors in solution self-assembly, interfacial self-assembly, and hybrid self-assembly.[19,20] Many impressive supramolecular aggregates and hybrids on all scales and dimensions, such as macroscopic tubes,[21] micro- or nanovesicles,[22,23] fibers,[24−26] spherical micelles,[27−29] large compound vesicles,[30] and honeycomb films,[31,32] have been generated. Nevertheless, the influencing factors to the self-assembly of HBPs are always restricted to the classical factors that also belong to the self-assembly of linear block polymers, such as hydrophilic/hydrophobic ratio, molecular weight, and copolymer composition.[33−35] In fact, supramolecular self-assembly of HBPs must be affected by characteristic factors such as DB. However, the effect of DB on the self-assembly of amphiphilic HBPs has not been studied up to now. We deduce that the difficulty to control the DB of HBPs blocks such a progress.

Previously, Hult et al.[36,37] and Penczek et al.[38,39] independently reported the synthesis of hyperbranched poly(3-ethyl-3-(hydroxymethyl)-oxetane) (PEHO). Subsequently, we found that DB of PEHO can be well controlled through the variation of reaction temperature.[40] Meanwhile, the molecular weight of PEHO did not change as reaction temperature varied. We also found that the amphiphilic multiarm copolymer PEHO-*star*-PEO, with a hyperbranched PEHO core and many linear polyethylene oxide (PEO) arms, can self-assemble into several kinds of supramolecular structures.[21−23] These previous works motivate us to synthesize a series of PEHO-*star*-PEOs with DB-variable but molecular-weight-analogous PEHO cores and similar PEO arms, through which we can carefully explore the relationship between DB and self-assembly behaviors thereof. The results indicate that the self-assembly morphology of PEHO-*star*-PEOs can be controlled from vesicles, wormlike micelles, to spherical micelles through the adjustment of the DB of PEHO core, and a self-assembly mechanism based on the packing parameter was provided to elaborate the relationship.

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Experimental Section

The details of the experiments were provided in the Experimental Section of the Supporting Information.

Results and Discussion

As shown in Scheme 1, the amphiphilic multiarm copolymer of PEHO-*star*-PEOs was obtained by the sequential cationic ring-opening polymerizations of 3-ethyl-3-(hydroxymethyl)-oxetane (EHO) and ethylene oxide (EO) in the presence of $BF_3 \cdot Et_2O$.[21−23] Several PEHO-*star*-PEO samples having a PEHO core with similar molecular weight but different DB and similar PEO arms were synthesized. As indicated, PEHO-*star*-PEO with linear PEHO core possesses a comblike structure, whereas PEHO-*star*-PEO with hyperbranched PEHO core possesses a core−shell structure. The DB of PEHO core was controlled by changing reaction temperature from 25 to −50 °C on the step of cationic ring-opening polymerization of EHO.[40] During the polymerization, a small amount of PEHO sample was picked up for characterization before reacting with EO. One of the quantitative ^{13}C NMR spectra of PEHO samples is given in Figure S1 of the Supporting Information, in which the three peaks near 22.50 ppm are attributed to the carbon atoms of methylene in the ethyl groups of the dendritic unit (*D*), the linear unit (*L*), and the terminal unit (*T*).[37] The three peaks near 22.50 ppm are magnified (Figure 1) for the convenience of DB calculation. To compare with each other, the peaks of *L* units were normalized to the same intensity, so the obvious decrease in the peaks attributed to *D* units and *T* units strongly indicates the successful syntheses of PEHO cores with decreasing DB. We determined the resultant DB by using the equation $DB = 2D/(2D + L)$, as reported by Frey.[3,4] The molar ratio of the EO units (in PEO arms) to the EHO units (in PEHO core) symbolized by $R_{A/C}$ was determined by means of ^1H NMR (Figure S2 in the Supporting Information). The modification degree (*J*) of hydroxy group in the PEHO core was determined by means of quantitative ^{13}C NMR (Figure S3 in the Supporting Information), which indicates that almost all of the hydroxy groups in the PEHO core are reacted during the copolymerization. The number-average molecular weight (M_n) of PEHO-*star*-PEO samples and corresponding PEHO core samples was characterized by SEC (Figure S4 in the Supporting Information). All details of characterization experiments are shown in the Supporting Information, and the results are listed in Table 1. As shown in Table 1, the M_n and $R_{A/C}$ of the obtained PEHO-*star*-PEO samples (HP1-4) are considered to be roughly

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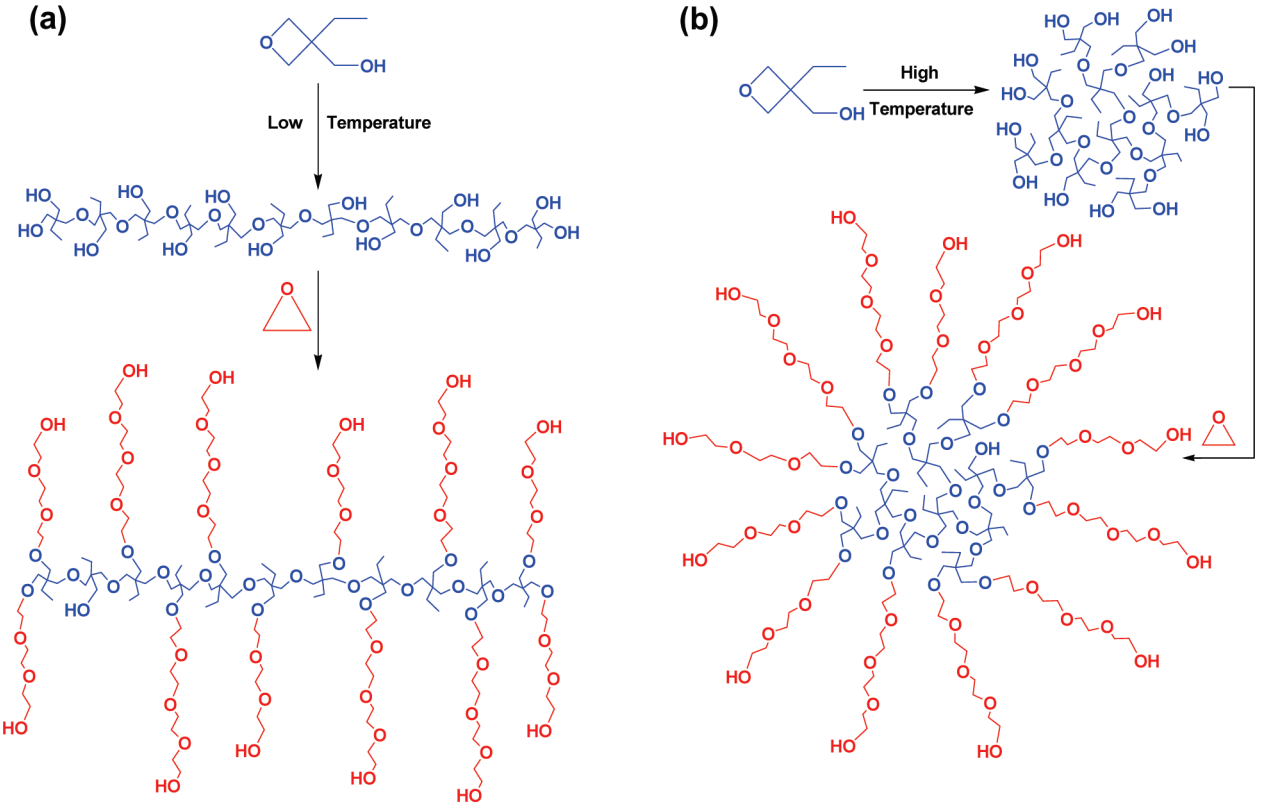
Scheme 1. Preparation of PEHO-*star*-PEO with (a) Linear or (b) Highly Branched PEHO Core



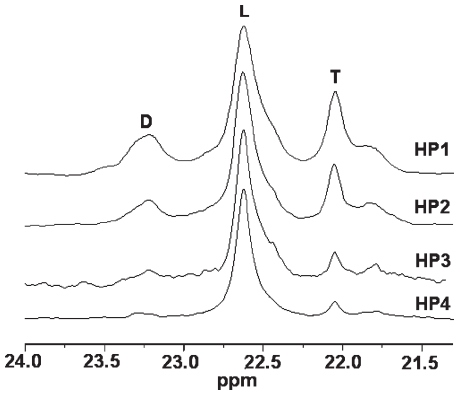


Figure 1. Variation of the three peaks near 22.50 ppm in quantitative ^{13}C NMR spectra of PEHO samples.

the same as each other. It should be noticed that every PEO arm in the copolymer has nearly four EO repeating units, so the self-assembly behavior of the copolymer will be significantly affected by the structure of the PEHO core because of such short PEO arms.

The solution self-assembly behaviors of the obtained polymer samples were carefully evaluated. Although the water solubility of PEHO-*star*-PEOs with high DB of PEHO core is very good, it is not good enough for the samples with low DB. Therefore, the method reported by Eisenberg et al. to create "crew-cut" aggregates[16,42] was utilized for the self-assembly of all PEHO-*star*-PEO samples, which involves the dissolution of the samples in the cosolvent of DMSO, followed by the dialysis against water around 8 °C to remove the organic solvent. Such a low temperature is far below the lower critical solution temperature (LCST) of all samples.[23] The details of self-assembly process are described in the Supporting Information, and the final polymer concentration of all samples is 2 mg/mL.

TEM, SEM, and cryo-TEM were used to observe directly the morphology of the self-assembly objects. The photographs obtained by TEM and SEM measurements are shown in Figures 2 and 3, respectively. Figure 2a shows the TEM image of HP1 sample negatively stained by uranyl acetate (2 wt %). The contrast difference between the aggregate skin (white arrows) and the inner pool proved that the aggregates were vesicular in nature.[43−45] The vesicles partially deformed in morphology because of the evaporation of the water during the preparation of TEM samples. Figure 3a is the SEM image of HP1 aggregates, which were totally collapsed on the substrate to form flattened shape with rounded edges and a slightly concave top surface. Therefore, both the TEM and SEM measurements support the fact that HP1 polymers self-assemble into vesicles in water. Such a result agrees fairly well with our previous work,[22,23] in which we found PEHO-*star*-PEOs with relatively high DB (∼0.4) of PEHO core can directly assemble into polymer vesicles in water. Figures 2b and 3b show the TEM and the SEM images of HP2 aggregates, respectively, which indicate the formation of wormlike micelles. Like other usual wormlike micelles,[46,47] the present micelles are bent and soft rather than straight and stiff. Also, the images suggest a relatively narrow size distribution of the micelles diameters but a widely variable length. For HP3 and HP4 samples, TEM images (Figures 2c, 2d) show the formation of solid and spherical micelles. Figure 3c,d shows the corresponding SEM images. Unlike the flattened vesicle structure, as shown in Figure 3a, HP3 and HP4 aggregates maintain the spherical shape and are convex on the substrate, which provides more evidence of the formation of micelles. Although the resolution of cryo-TEM images is not very good, the results (Figure S5 in the Supporting Information) clearly support the fact that the polymer samples self-assemble into vesicles for HP1, wormlike micelles for HP2, and spherical micelles for HP3 and HP4.

The average diameters of HP1 vesicles, HP2 wormlike micelles, and HP3 and HP4 spherical micelles were calculated by a

Table 1. Characterizations of PEHO-*star*-PEO Samples and Assemblies

sample	reaction temp (°C)[a]	R_{feed}[b]	DB_{core} (%)	R_{feed}[c]	$R_{A/C}$[d]	$M_{n,core}$[e]	$M_{n,sample}$[e]	D_{TEM} (nm)[f]	D_{SEM} (nm)[g]
HP1	25	2	44	4:1	3.4	3100	6600	161 ± 65	159 ± 66
HP2	15	2	33	4:1	3.6	4000	7100	45 ± 15	42 ± 9
HP3	−25	2	20	4:1	3.4	4100	7500	45 ± 11	41 ± 5
HP4	−50	50	5	4:1	3.7	3000	6100	154 ± 37	139 ± 32

[a] Reaction temperature for the synthesis of PEHO cores. [b] R_{feed} is the feed ratio of EHO monomer to catalyst for the synthesis of PEHO cores. (For HP4, R_{feed} changed to 50 to obtain PEHO core with lower DB.[41]) [c] R_{feed} is the feed ratio of EO to EHO monomer. [d] $R_{A/C}$ is the molar ratio of the EO units (in PEO arms) to the EHO units (in PEHO core), determined by ^{1}H NMR. [e] Determined by SEC. [f] Determined from TEM photographs. [g] Determined from SEM photographs.

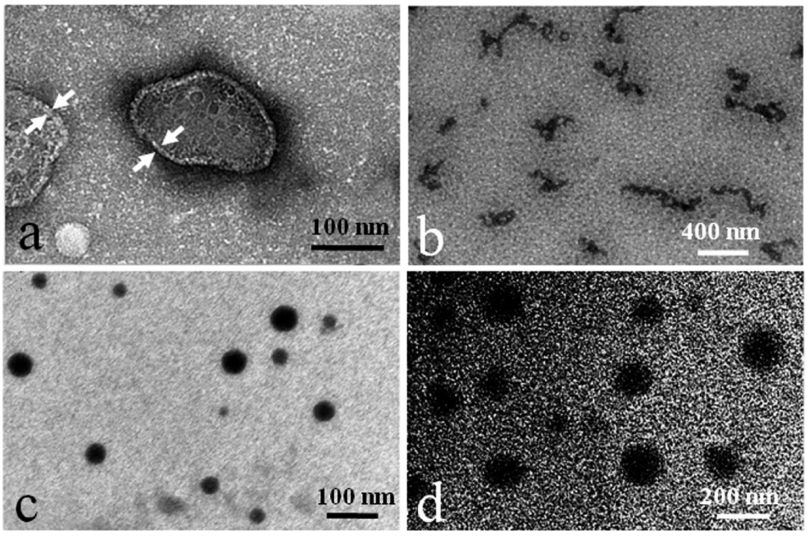


Figure 2. TEM photographs of PEHO-*star*-PEO assemblies: (a) HP1 vesicles, (b) HP2 wormlike micelles, (c) HP3 micelles, and (d) HP4 micelles.

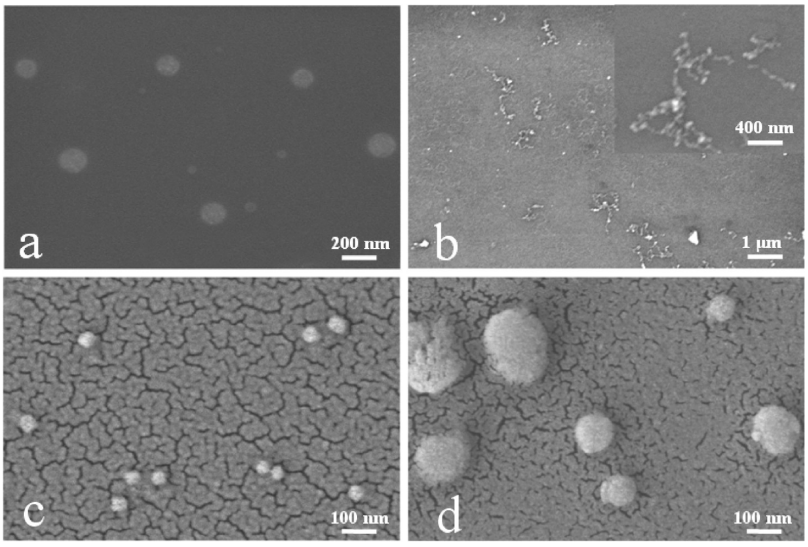


Figure 3. SEM photographs of PEHO-*star*-PEO assemblies: (a) HP1 vesicles, (b) HP2 wormlike micelles, (c) HP3 micelles, and (d) HP4 micelles. The inset in part b shows another magnified view of wormlike micelles.

statistical analysis of > 50 particles in TEM or SEM photos for every sample, and the obtained D_{TEM} and D_{SEM} are listed together in Table 1, which are in good agreement with each other. As shown in Table 1, the diameter of HP1 vesicles is ~160 nm. It should be noted that the HP1 sample will self-assemble into microsized vesicles at the temperature near the LCST.[23] Therefore, to avoid the influence of the LCST transition, the self-assembly temperature was set around 8 °C, and only the nanosized vesicles were obtained. The wall thickness is another important parameter to characterize the vesicles. The TEM image (Figure 2a) shows that the average thickness of a vesicle wall is ~7.1 nm. The AFM image (Figure 4a) shows that HP1 aggregates have the flattened shape with rounded edges, and the average height of the particles is ~13.4 nm, which further proves a collapsed vesicle structure, as shown in the cross-section model (Figure 4a, inset).[48] Therefore, we can get the average wall thickness of 6.7 nm from the AFM measurement, which agrees well with the TEM result. It should be noted that the average vesicle wall thickness from CTEM is ~16.9 nm, which is larger than TEM and AFM results. Such a discrepancy should be attributed to the hydrated state of vesicles in the CTEM measurement and the dehydrated (or collapsed) state in TEM and AFM

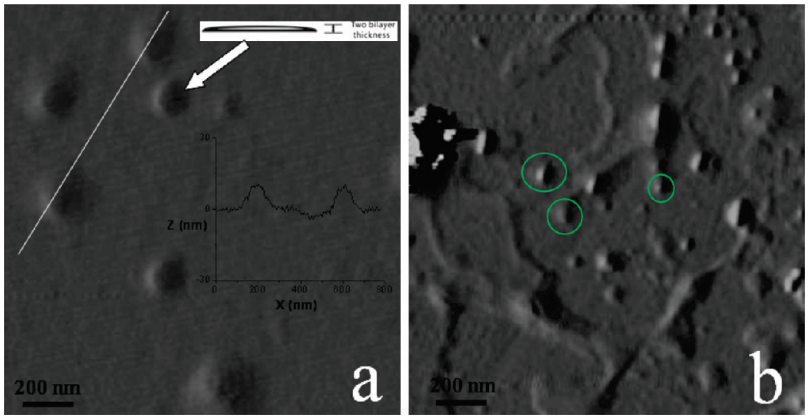


Figure 4. AFM images of (a) HP1 vesicles and (b) HP2 wormlike micelles. The insets in part a show the height curve graph of two vesicles marked with a white line and a cross-section model of the collapsed vesicle structure.

measurements. Compared with the molecular size and the vesicle wall thickness, we deduce that the HP1 polymer vesicles possess a bilayer structure.

It is interesting to note that the diameter of HP2 wormlike micelles is almost similar to that of HP3 spherical micelles, which may hint at a relationship between them in the self-assembly mechanism. Previously, Wooley et al.[49] have reported a rod-to-sphere phase transition for the formation of spherical micelles from rod micelles. We speculate that it is also the case in the formation of HP3 micelles. The AFM image of the HP2 sample (Figure 4b) provides the intermediates to support the speculation well. As shown, HP2 polymers do self-assemble into wormlike micelles with a diameter of 42 nm. Interestingly, a few spherical micelles that possess similar diameter with wormlike micelles are observed, and some of them are located at the end of the wormlike micelles (green circles), which proves the reliability of the rod-to-sphere transition.

The diameter of HP4 micelles is much larger than that of HP3 micelles. As shown in Scheme 1, PEHO-*star*-PEO with a higher DB is more core−shell-like, and thus the interactions between PEHO cores and water are enhanced by the arms. In other words, the PEHO cores are relatively more hydrophobic in PEHO-*star*-PEOs with a lower DB than those with a higher DB because of the changes in the shielding with the PEO arms. Therefore, we infer that HP4 micelles are constructed from the aggregation of small micelles such as HP3 micelles driven by the enhanced hydrophobic interaction. Previously, the large micelles >100 nm, self-assembled from amphiphilic hyperbranched multiarm copolymers, have already been constructed through the secondary aggregation of small micelles or unimolecular micelles, which is called the multimicelle aggregate (MMA).[27,50−55] We believe that the HP4 micelles presented here are a kind of MMA with the basic building units of small micelles.

On the basis of the results above, we can sum up that DB is an essential factor for the self-assembly of amphiphilic hyperbranched multiarm copolymers. The self-assemblies of PEHO-*star*-PEOs from vesicles, wormlike micelles to spherical micelle, are governed by different DB in PEHO cores from 44 to 5%. Now, the question is why the morphology depends on DB? It is known that the shape of self-assembled structures formed by amphiphiles is governed by their geometry. This connection is usually expressed in terms of the packing parameter ρ (also called the shape factor), defined by $\rho = v/al$, where v is the hydrophobic volume of the amphiphile, a is the interfacial area, and l is the chain length normal to the interface.[56,57] As the value of ρ increases, spherical ($\rho = 1/3$), cylindrical ($\rho = 1/2$), and bilayer structures ($\rho = 1$) are formed. Previously, we found that the theory of the packing parameter is also suitable for the self-assembly behaviors of amphiphilic HBPs.[58]

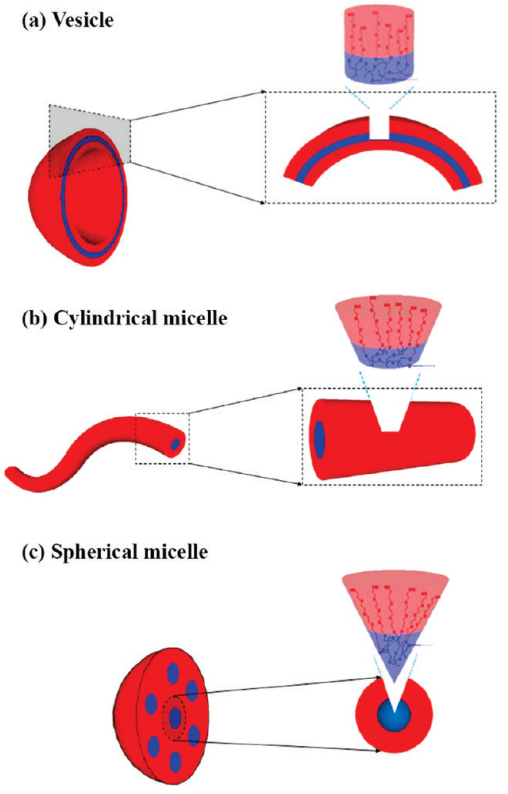


Figure 5. Diagrammatic sketch of the molecular packing models in the assemblies from PEHO-*star*-PEOs with different DB: (a) model for HP1 vesicle, (b) model for HP2 cylindrical micelle, and (c) model for HP3/HP4 spherical micelle.

For PEHO-*star*-PEOs, water is the selective solvent of PEO arms, so PEO arms are hydrophilic, whereas the PEHO core is hydrophobic. Here as DB of PEHO core changes, l remains basically constant because of the similar PEO chain length, and v is also constant because of the fixed molecular weight of PEHO core; therefore, the packing parameter ρ is only determined by a. Evidently, as DB goes down, the structure of the PEHO tecton changes from globular to linear (scheme 1), so the interfacial area, a, increases for a given PEHO volume, which leads to the decrease in the packing parameter, ρ. Therefore, PEHO-*star*-PEOs with a high DB of PEHO core and a so-induced high ρ form vesicles in water, whereas those with a mid DB and a so-induced mid ρ tend to form cylindrical micelles, and those with a low DB and a so-induced low ρ form spherical micelles. Antonietti and Förster[56] have pointed out

that the polymer tectons with many branch points are inclined to form bilayer structures because of the low conformational entropy, which supports our findings from another aspect.

As described above, we can speculate the self-assembly mechanism depending on the DB of PEHO cores (Figure 5). For the PEHO-*star*-PEO copolymers with a high DB such as the HP1 sample, the packing parameter, ρ, is close to 1, and thus the highly branched copolymers spontaneously segregate into a cylinder shape[59] and self-assemble into vesicles (Figure 5a). For the HP2 sample, the DB decreases, and the ρ decreases close to 1/2. The molecular geometry is thus altered from a cylinder to a trapezoidal cylinder, leading to the formation of cylindrical micelles (Figure 5b). Further decrease in DB and thus the ρ (HP3/HP4 samples) causes a cone molecular geometry, leading to the formation of spherical micelles (Figure 5c). As mentioned above, the large HP4 spherical micelles may possess an MMA structure consisting of small micelles.

Conclusions

In conclusion, we have successfully prepared a series of amphiphilic hyperbranched multiarm copolymer PEHO-*star*-PEOs, which possess different DB in PEHO core. The copolymers can self-assemble into vesicles, wormlike micelles, and spherical micelles with the decrease in the DB, respectively. The findings will contribute to new fundamental understanding in the relationship between the molecular structures and the self-assemblies of HBPs. Intuitively, amphiphilic hyperbranched multiarm copolymers tend to form unimolecular micelles or fibers. However, hitherto, many delicate supramolecular structures have been reported from the self-assembly of amphiphilic HBPs. Evidently, there are some specialties in the self-assembly of HBPs to afford the morphological complexity, and the DB dependence may be the most important one among them.

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Supporting Information Available: Experimental section, characterizations of PEHO-*star*-PEOs with different DB of PEHO core, and CTEM photographs of PEHO-*star*-PEO assemblies. This material is available free of charge via the Internet at http://pubs.acs.org.

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