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# Effect of architectural asymmetry of hyperbranched block copolymers on their phase boundaries†

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Asymmetric architecture of AB-type block copolymers can induce additional spontaneous curvature to the A/B interface, accordingly deflecting the phase boundaries. However, it is often difficult to determine or compare the asymmetric effects of different asymmetric architectures. In this work, we proposed to use the equivalent arm number  $n_{\text{equ}}$ , which was originally defined as  $n_{\text{equ}} = n/iD$  for  $AB_n$  with unequal B-arms and  $iD$  being the intramolecular polydispersity of these B-arms, to quantify the asymmetric effect of various linear-hyperbranched copolymers. For each linear-hyperbranched copolymer,  $n_{\text{equ}}$  is estimated by matching its phase boundaries on the side with expanded spherical phase region with those of  $AB_n$  with unequal B-arms but tunable  $iD$ . Our results suggest that the addition of B-blocks at the further location from the A–B joint point has less influence on  $n_{\text{equ}}$ , i.e. the asymmetric effect, because these B-blocks can access more space. For the linear-dendrimer copolymers,  $n_{\text{equ}}$  changes from 2 to about 3.8 when the overall generation number of the copolymer increases from 2 to 5. In other words, the asymmetric effect of these linear-dendrimer copolymers is intermediate between those of  $AB_2$  and  $AB_4$  miktoarm star copolymers. In brief,  $n_{\text{equ}}$  can effectively describe the asymmetric effect on the interfacial curvature of complex asymmetric architectures.

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## 1 Introduction

Block copolymers can self-assemble into innumerable ordered structures when varying their composition and architectures,<sup>1–9</sup> and thus have attracted abiding interest<sup>10–16</sup> in many fields including functional nanomaterials and nanotechnology.<sup>17–20</sup> AB diblock copolymers as the simplest block copolymer can form sphere, cylinder, network and lamellar structures as their composition changes from asymmetric to symmetric.<sup>21–30</sup> If there are no other different properties between A and B blocks in the AB diblock, the phase diagram with respect to the composition (or the volume fraction of A-block,  $f$ ) is symmetric.<sup>31</sup> On both sides of the symmetric phase diagram, the spherical phase region is rather narrow and is mainly occupied by the body-centered cubic (BCC) phase. To expand the spherical region, an additional asymmetry factor needs to be introduced, such as the conformational asymmetry<sup>32–38</sup> or architectural asymmetry.<sup>39–49</sup> One of the common asymmetric

architectures is  $AB_n$  miktoarm star copolymers composed of a single A block connected with  $n$  B blocks.<sup>47,48,50–52</sup> The multiple B blocks are more difficult to be stretched than the single A block, creating a tendency for the A/B interface to curve toward the A block. In other words, a curvature effect is caused by the branching architecture in addition to that arising from the compositional asymmetry. As a result, the phase diagram becomes asymmetric and is deflected to large volume fraction  $f$  of the A-block, of which the phase region of the A-sphere is expanded while that of the B-sphere is compressed. More importantly, the complex Frank–Kasper  $\sigma$  or A15 phase is stabilized with the expansion of the spherical region.<sup>42,47,53–55</sup>

Conformational asymmetry is related to the different intrinsic properties of flexibility, which can also be encoded into the asymmetry of the phase diagram. Almdal *et al.* proposed the ratio of Kuhn length  $b_A/b_B$  to describe the conformational asymmetry of the linear AB diblock by comparing the radius of gyration ( $R_g$ ) of the linear A-block and B-block.<sup>32</sup> The asymmetry parameter of the AB diblock was updated as  $\rho_A b_A^2/\rho_B b_B^2$ , where  $\rho_\kappa$  ( $\kappa = A$  or  $B$ ) is the density of the  $\kappa$ -monomer.<sup>33,56</sup> Soon after, Milner combined conformational asymmetry and architectural asymmetry into an asymmetry parameter,  $\varepsilon \equiv (n_B/n_A)(\rho_A b_A^2/\rho_B b_B^2)^{0.5}$ , in an AB-type miktoarm star copolymer composed of  $n_A$  A-arms and  $n_B$  B-arms.<sup>50</sup> This unified definition implies that the ratio of arm numbers and that of Kuhn lengths should have a similar effect

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on the phase behavior, which has been confirmed in subsequent experimental<sup>57–60</sup> and theoretical studies.<sup>37,43,48</sup>

Besides the miktoarm star architectures, there are many other asymmetric architectures, and for some of them it is difficult to judge their degree of asymmetry (*e.g.* their deflection degree to the phase diagram). Some effort has been devoted to quantifying the asymmetry degrees of various complex AB-type block copolymers.<sup>44,51,61–63</sup> For example, Fredrickson *et al.*<sup>44</sup> attempted to calculate the asymmetry parameter of comblike/bottlebrush block copolymers by approximately computing the radius of gyration of the A and B blocks. Their asymmetry parameter can describe the deflection degree to the phase diagram for the comblike copolymers well, but not for the bottlebrush copolymers. In our previous work,<sup>51</sup> we proposed the number of equivalent (or effective) arms ( $n_{\text{equ}}$ ) as an asymmetry parameter with reference to  $AB_n$  miktoarm star copolymers of equal arms, and used it to quantify the deflection degree of the phase diagrams of  $AB_n$  of unequal arms. We found that  $n_{\text{equ}}$  can be simply expressed as  $n_{\text{equ}} = n/iD$ , where  $iD$  represents the intramolecular polydispersity of the multiple arms. Our self-consistent field theory (SCFT) results demonstrate that various  $AB_n$  of unequal arms with different  $n$  but with equal  $n_{\text{equ}}$  exhibit very similar asymmetric phase diagrams, verifying that  $n_{\text{equ}}$  is an efficient asymmetry parameter for measuring the effect of asymmetric architectures on the deflection of the phase diagrams. In line with Milner's description,<sup>50</sup> we can combine conformational asymmetry with architectural asymmetry, then modify the equation for determining the equivalent  $\varepsilon$  ( $\varepsilon_{\text{equ}}$ ) of linear-hyperbranched copolymers:  $\varepsilon_{\text{equ}} = n_{\text{equ}}(\rho_A b_A^2/\rho_B b_B^2)^{0.5}$ . For the linear-hyperbranched copolymers studied in this paper, we set  $\rho_A = \rho_B$  and  $b_A = b_B$ , thus  $n_{\text{equ}} = \varepsilon_{\text{equ}}$ . The  $n_{\text{equ}}(\varepsilon_{\text{equ}})$  is mainly reflected in the change of spontaneous curvature for the AB-type copolymer, and the most prominent manifestation is its influence on the sphere/cylinder phase boundary. Therefore, in this work, we attempt to extend the concept of  $n_{\text{equ}}$  to other asymmetric block copolymers to quantify their architectural asymmetry.

Hyperbranched copolymers including dendrimer-like have been extensively studied due to their unique architectures.<sup>42,46,64–78</sup> Grason *et al.*<sup>42,46</sup> proposed that the block copolymer composed of linear A-block and hyperbranched B-blocks exhibits a significantly amplified effect of spontaneous curvature toward the A-domain. As a result, the phase boundaries of these linear-hyperbranched copolymers are notably deflected to large volume fraction of the A-block ( $f$ ), and the Frank-Kasper spherical A15 phase was predicted to be stable in the expanded region of the A-sphere.<sup>42,47</sup> Although the architectures are notably asymmetric, it is still difficult to determine how large their asymmetry degrees are, for example by comparing them with those of  $AB_n$  miktoarm star architectures. In this work, we will determine the equivalent arm number  $n_{\text{equ}}$  by comparing the phase boundaries of various hyperbranched copolymers to those of different  $AB_n$  with equal or unequal arms using SCFT. We first move the two B-arms of the equal-arm- $AB_4$  or unequal-arm- $AB_4$  architecture along the other two B-arms to obtain a series of linear-hyperbranched block copolymers (Fig. 1), thus determining their  $n_{\text{equ}}$ . With the arm length ratios of 1 : 1 : 2 : 2,

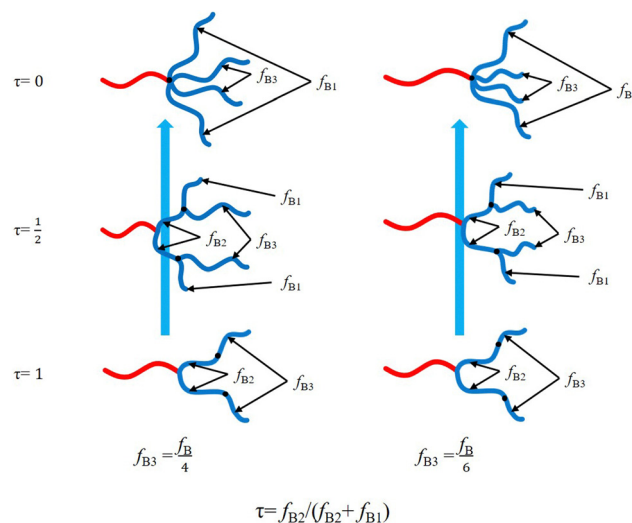


Fig. 1 Schematics of the linear-hyperbranched architectures generated from  $AB_n$  with equal or unequal B arms.

the ideal linear-dendrimer architecture can be generated from  $AB_4$  when the two short B-arms are moved to the middle points of the other two B-arms, respectively. Then we propose a simple expression for  $n_{\text{equ}}$  with respect to the tethering position, which can reasonably measure the asymmetry degrees of these different linear-hyperbranched copolymers.

## 2 Theory and method

We consider an incompressible melt of volume  $V$  consisting of  $n_C$  chains of hyperbranched copolymers or  $AB_n$ . To give prominence to the architectural effect on the self-assembly behavior, we simply assume that all segments have the same Kuhn length  $b$  and density  $\rho_0$ . Each copolymer is composed of  $N$  segments in total, of which the A-block contains  $fN$  segments. Within the framework of SCFT for the Gaussian chain, the free energy functional per chain at temperature  $T$  is given by<sup>79,80</sup>

$$\frac{F}{n_C k_B T} = -\ln Q + \frac{1}{V} \int d\mathbf{r} \{ \chi N \phi_A(\mathbf{r}) \phi_B(\mathbf{r}) - w_A(\mathbf{r}) \phi_A(\mathbf{r}) - w_B(\mathbf{r}) \phi_B(\mathbf{r}) - \xi(\mathbf{r}) [1 - \phi_A(\mathbf{r}) - \phi_B(\mathbf{r})] \} \quad (1)$$

where  $k_B$  is the Boltzmann constant.  $\phi_\kappa(\mathbf{r})$  and  $w_\kappa(\mathbf{r})$  ( $\kappa = A, B$ ) are the volume-fraction function and the conjugate potential field of the  $\kappa$ -component, respectively.  $\xi(\mathbf{r})$  is a Lagrange multiplier used to enforce the incompressibility condition,  $\phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) = 1$ . The quantity  $Q$  is the partition function of one single chain interacting with the mean fields of  $w_\kappa(\mathbf{r})$  ( $\kappa = A, B$ ), which is determined by

$$Q = \frac{1}{V} \int d\mathbf{r} q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) \quad (2)$$

where  $q(\mathbf{r}, s)$  and  $q^\dagger(\mathbf{r}, s)$  are two conjugate propagator functions satisfying the modified diffusion equations

$$\frac{\partial q(\mathbf{r}, s)}{\partial s} = \nabla^2 q(\mathbf{r}, s) - w(\mathbf{r}, s) q(\mathbf{r}, s) \quad (3)$$



$$-\frac{\partial q^\dagger(\mathbf{r}, s)}{\partial s} = \nabla^2 q^\dagger(\mathbf{r}, s) - w(\mathbf{r}, s)q^\dagger(\mathbf{r}, s) \quad (4)$$

where  $w(\mathbf{r}, s) = w_\kappa(\mathbf{r})$  when  $s$  belongs to the  $\kappa$ -block ( $\kappa = \text{A, B}$ ). The values of  $q(\mathbf{r}, s)$  or  $q^\dagger(\mathbf{r}, s)$  at the free ends are set to 1 as the initial conditions. The spatial length is rescaled by the radius of gyration ( $R_g$ ) of an unperturbed linear homopolymer chain with  $N$  segments,  $R_g = N^{1/2}b/\sqrt{6}$ . We considered that A and B segments have the same segment density ( $\rho_A = \rho_B$ ) and length ( $b_A = b_B$ ). The total number of segments in the A block and B blocks is given by  $f_A N$  ( $f_A = f$ ) and  $f_B N$ , respectively. Minimization of the free energy functional with respect to the volume-fraction functions and the mean fields leads to the following SCFT equations

$$w_A(\mathbf{r}) = \chi N \phi_B(\mathbf{r}) + \xi(\mathbf{r}) \quad (5)$$

$$w_B(\mathbf{r}) = \chi N \phi_A(\mathbf{r}) + \xi(\mathbf{r}) \quad (6)$$

$$\phi_A(\mathbf{r}) = \frac{1}{Q} \int_{s \in A} ds q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) \quad (7)$$

$$\phi_B(\mathbf{r}) = \frac{1}{Q} \int_{s \in B} ds q(\mathbf{r}, s) q^\dagger(\mathbf{r}, s) \quad (8)$$

$$1 = \phi_A(\mathbf{r}) + \phi_B(\mathbf{r}) \quad (9)$$

We use the pseudospectral method<sup>81–83</sup> to solve the modified diffusion equations, and implement the Anderson mixing iteration scheme<sup>84</sup> to accelerate the converging process toward the equilibrium solution. We consider eight ordered phases, including face-centered cubic (FCC) spherical phase, body-centered cubic (BCC) spherical phase, Frank–Kasper  $\sigma/\text{A15}$  spherical phase, hexagonal cylinder phase ( $C_6$ ),  $Fddd$  network phase ( $O^{70}$ ), double-gyroid network phase (G) and lamellar phase (L) (Fig. 2). It is necessary to mention that we do not consider the hexagonally close-packed (HCP) spherical phase because it is nearly degenerate with the FCC phase. The sizes of the unit cell ( $l_x$ ,  $l_y$  and  $l_z$ ) are optimized by the variable cell algorithm.<sup>85–87</sup> The chain contour is divided into pieces with  $\Delta s \leq 0.005$ . The grid spacings  $\Delta x$ ,  $\Delta y$  and  $\Delta z$  are chosen to be smaller than  $0.15R_g$  by

using a lattice of  $64 \times 64 \times 64$  for the three-dimensional phases except for a lattice of  $256 \times 256 \times 128$  for the  $\sigma$  phase and a lattice of  $32 \times 64 \times 128$  for the  $O^{70}$  phase. In addition, the pseudospectral method is accelerated using the crystallographic FFT to replace the normal FFT.<sup>88</sup>

### 3 Results and discussion

We first consider a linear-hyperbranched architecture composed of a linear A-block connected with two generations of hyperbranched B-blocks. As shown in Fig. 1, this copolymer can be seen as an  $\text{AB}_2$  copolymer tethered by an additional B-block on each branching B-block. The tethering B-block with volume fraction of  $f_{B3}$  divides the branching B-block of  $\text{AB}_2$  into two sub-blocks denoted as B1 (with free end) and B2 (connected with A block) blocks with volume fractions  $f_{B1}$  and  $f_{B2}$ , respectively. We introduce a variable  $\tau = f_{B2}/(f_{B2} + f_{B1})$  to characterize the tethering position of the B3-block. Accordingly, the linear-hyperbranched copolymer is reduced to  $\text{AB}_2$  with two equal B-arms at  $\tau = 1$  and  $\text{AB}_4$  with equal or unequal B-arms at  $\tau = 0$ , respectively. The simple analysis implies that the asymmetry degree of this complex architecture should lie between those of  $\text{AB}_2$  and  $\text{AB}_4$  copolymers.

Besides the tethering position, another characteristic parameter is the ratio of B3-block. In this work, we consider two specific cases:  $f_{B3} = f_B/4$  and  $f_{B3} = f_B/6$ . In the first case of  $f_{B3} = f_B/4$ , the linear-hyperbranched architecture is reduced to  $\text{AB}_4$  of equal arms. In the other case of  $f_{B3} = f_B/6$ , the architecture of the B-blocks becomes dendrimer-like at  $\tau = 1/2$ .

To demonstrate the change of the architecture on the asymmetry, we vary  $\tau$  (*i.e.* the tethering position of B3-block) to gradually change the linear-hyperbranched architecture and construct the phase diagrams with respect to  $f$  and  $\chi N$ . Fig. 3 presents the phase diagrams of the linear-hyperbranched copolymer with  $f_{B3} = f_B/4$  for  $\tau = 0$ ,  $\tau = 1/3$ ,  $\tau = 2/3$  and  $\tau = 1$ , respectively. At  $\tau = 0$ , the copolymer is  $\text{AB}_4$  of equal arms, and thus its phase diagram is rather largely deflected to large  $f$ . Accordingly, the overall phase region of the A-sphere is expanded to range from  $f \approx 0.172$  to  $f \approx 0.344$  with a width of about  $\Delta f \approx 0.172$  at  $\chi N = 40$ , consisting of a wide window of Frank–Kasper  $\sigma$ -phase as well as a considerable window of A15-phase. As the two B3-blocks (two of B-arms) move away from the junction point to the tethering positions of  $\tau = 1/3$ , the asymmetry of the phase diagram is noticeably reduced, accompanied by a narrowing of the A-spherical phase region. In particular, the width of the A15-phase window is decreased from  $\Delta f \approx 0.041$  at  $\tau = 0$  to  $\Delta f \approx 0.018$  at  $\tau = 1/3$ . When the B3-blocks move to  $\tau = 2/3$ , the asymmetry or deflection of the phase diagram is further decreased, leading to the absence of the A15-phase region. Finally, the architecture changes to  $\text{AB}_2$  at  $\tau = 1$ , whose phase diagram is considerably less asymmetric than that of  $\text{AB}_4$  at  $\tau = 0$ . The width of the A-spherical phase region at  $\chi N = 40$  is narrowed to be  $\Delta f \approx 0.127$ .

Qualitatively, the decrease in the asymmetry of the phase diagram with increasing  $\tau$  can be explained by the change in the overall extension distance<sup>8</sup> of the B-blocks from the A/B

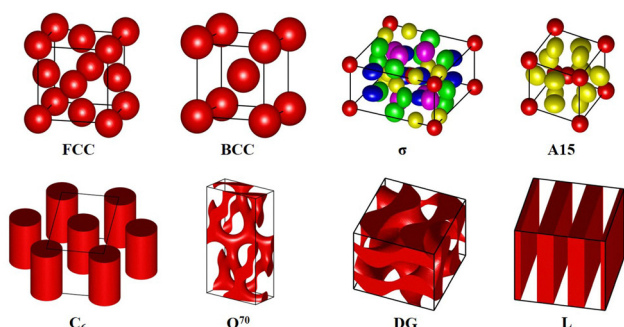


Fig. 2 Isosurface plots of the candidate ordered phases considered in the current study, including FCC, BCC,  $\sigma$ , A15, hexagonally arranged cylinders ( $C_6$ ),  $Fddd$  network ( $O^{70}$ ), double-gyroid (G) and lamellae (L). Larger and clearer figures and specific parameters are provided in the ESI.†





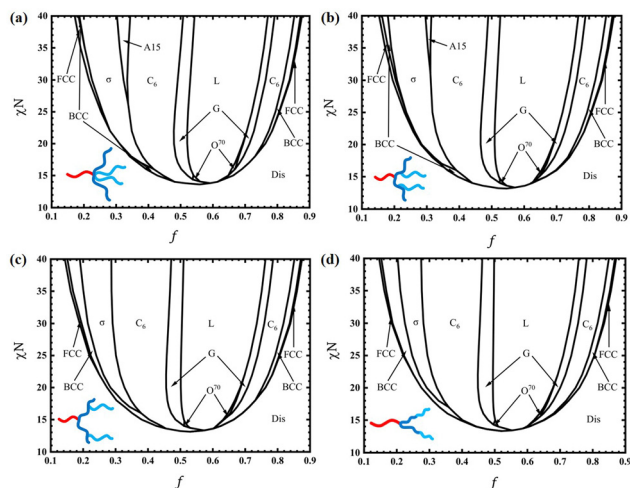


Fig. 3 Phase diagrams for copolymers with (a)  $\tau = 0$ , (b)  $\tau = 1/3$ , (c)  $\tau = 2/3$ , and (d)  $\tau = 1$ . In all cases,  $f_{B3} = f_B/4$ .

interface to the central area of the B-domain. Obviously, as the B3-blocks move from the junction point toward the free ends of the B1-blocks, the extension distance of the B-blocks increases, lowering the tendency of the B-blocks to locate outside the curvature. In other words, the effect of spontaneous curvature bending toward the A-domain is reduced with increasing  $\tau$ , lowering the asymmetry of the phase diagram. In order to quantify the change in the asymmetry of the phase diagram with  $\tau$ , we attempt to estimate the equivalent number of arms ( $n_{\text{equ}}$ <sup>51</sup>) by comparing the phase boundaries of the linear-hyperbranched copolymer with those of  $AB_n$  of unequal B arms. As the linear-hyperbranched architecture changes from  $AB_4$  to  $AB_2$  as  $\tau$  increases from 0 to 1, its  $n_{\text{equ}}$  should accordingly decrease from 4 to 2. Therefore, we choose  $n = 4$  and consider four arms containing two equal long arms with a segment number of  $f_{B1}N$  and two equal short arms with a segment number of  $f_{B3}N$ . By tuning the relative lengths of the long and short arms of  $AB_4$ , we can get any value of  $n_{\text{equ}} = n/iD$ , where  $iD = 2(k^2 + 1)/(k + 1)^2$  is the intramolecular polydispersity index<sup>51</sup> of the four arms of  $AB_4$  with  $k = f_{B1}/f_{B3}$ . By minimizing the difference of the phase boundaries between the linear-hyperbranched copolymer with a given  $\tau$  and  $AB_4$  of unequal arms with respect to  $n_{\text{equ}}$  (or  $iD$ ), we can obtain the value of  $n_{\text{equ}}$  quantifying the asymmetry of the linear-hyperbranched copolymer.

When minimizing the difference of the phase boundaries in the phase diagrams with respect to  $f$  and  $\chi N$  between the linear-hyperbranched copolymer and the  $AB_4$  copolymer of unequal B arms with tunable  $n_{\text{equ}}$  or  $iD$ , we find it difficult to make all the boundaries between them perfectly consistent. The main reason is that the asymmetric architecture affects the deflection of different phase boundaries in different degrees. Accordingly, we estimate  $n_{\text{equ}}$  by mainly minimizing the sphere/cylinder, cylinder/gyroid and gyroid/lamella boundaries between the two copolymers in the region where A-blocks are located inside the curvature of the A/B interface, but not considering the sphere/disorder boundary. Fig. 4 presents the comparison of the phase diagrams between the linear-hyperbranched copolymer and the

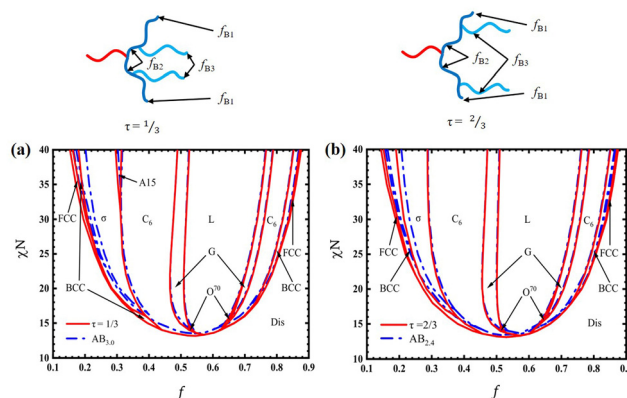


Fig. 4 Phase diagrams of: (a) the linear-hyperbranched copolymer with  $f_{B3} = f_B/4$  for  $\tau = 1/3$  (red solid) and  $AB_4$  copolymer with  $n_{\text{equ}} = 3.0$  (simply denoted as  $AB_{3.0}$ , blue dot-dashed lines); (b) the linear-hyperbranched copolymer with  $f_{B3} = f_B/4$  for  $\tau = 2/3$  (red solid) and  $AB_4$  copolymer with  $n_{\text{equ}} = 2.4$  (denoted as  $AB_{2.4}$ , blue dot-dashed lines). The length percentages of the B-blocks of all considered samples are listed in Table 2.

$AB_4$  copolymer of unequal B arms with optimized  $n_{\text{equ}}$  for  $\tau = 1/3$  and  $\tau = 2/3$ . For  $\tau = 1/3$ , the optimal  $n_{\text{equ}}$  is estimated around 3.0. In Fig. 4(a), the left  $C_6/G$  and  $G/L$  phase boundaries of the linear-hyperbranched copolymer with  $\tau = 1/3$  are nearly overlapped with those of  $AB_4$  with  $n_{\text{equ}} = 3.0$ , and the  $\sigma/A15$ ,  $\sigma/C_6$  and  $A15/C_6$  phase boundaries are also in good agreement with those of the latter. In contrast, the  $BCC/\sigma$ ,  $BCC/FCC$  and  $FCC/disorder$  boundaries between the two copolymers are noticeably different. Another factor that should not be ignored is the difference in the equivalent segregation strength<sup>89</sup> between the copolymers, which has a considerable influence on the order-disorder (ODT) transition boundaries.<sup>44,48</sup> Nevertheless, the overall agreement of the phase boundaries between the two copolymers is acceptable. Therefore, it is a feasible approach to quantify the asymmetry of the phase diagram of the complex linear-hyperbranched copolymer using the equivalent number of arms defined by  $AB_n$  of unequal B arms.

In Table 1, we estimate the values of  $n_{\text{equ}}$  for  $f_{B3} = f_B/4$  with  $\tau = 0.1, 0.2, \dots, 0.9$ . Fig. 5(a) suggests that  $n_{\text{equ}}$  decreases nonlinearly as  $\tau$  increases from 0 to 1. Since many phase boundaries need to be determined using SCFT for the estimation of each  $n_{\text{equ}}$ , the calculation is rather costly. To obtain the continuous value of  $n_{\text{equ}}$ , it would be useful to find an expression for  $n_{\text{equ}}$  as a function of  $\tau$ . According to the changing trend, we choose the following concise equation to calculate  $n_{\text{equ}}$  of linear-hyperbranched copolymers,

$$n_{\text{equ}} = n_{\text{min}} + \Delta n \times (1 - \tau)^\alpha, \quad (10)$$

where  $\Delta n = n_{\text{max}} - n_{\text{min}}$  and  $\tau = f_{B2}/(f_{B2} + f_{B1})$ . The copolymers with  $n_{\text{equ}} = n_{\text{max}} = 4$  and  $n_{\text{min}} = 2$  correspond to two limiting cases,  $\tau = 0$  and  $\tau = 1$ , respectively.  $\alpha$  is a constant that quantifies the nonlinear relationship between  $n_{\text{equ}}$  and  $\tau$ . By fitting the data points in Fig. 5(a) using the expression, we got  $\alpha \approx 1.6$ . As  $\tau$  decreases from 1 to 0, the increasing of  $n_{\text{equ}}$  along the fitting curve with  $\alpha = 1.6$  shown by the red solid lines in Fig. 5(a) is accelerating, causing the value of  $n_{\text{equ}}$  on the curve to be

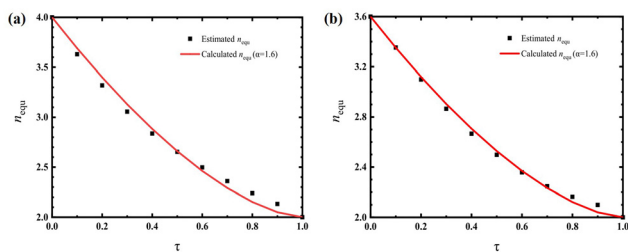


**Table 1** List of estimated  $n_{\text{equ}}$  and calculated  $n_{\text{equ}}$  for linear-hyperbranched copolymers with different  $\tau$ 

$f_{\text{B}3} = f_{\text{B}}/4$		
$\tau$	Estimated $n_{\text{equ}}$	$n_{\text{equ}}$ with $\alpha = 1.6$
0.1	3.63	3.69
0.2	3.32	3.40
0.3	3.06	3.13
0.4	2.84	2.88
0.5	2.65	2.66
0.6	2.50	2.46
0.7	2.36	2.29
0.8	2.24	2.15
0.9	2.13	2.05

$f_{\text{B}3} = f_{\text{B}}/6$		
$\tau$	Estimated $n_{\text{equ}}$	$n_{\text{equ}}$ with $\alpha = 1.6$
0.1	3.35	3.35
0.2	3.10	3.12
0.3	2.87	2.90
0.4	2.67	2.71
0.5	2.50	2.53
0.6	2.36	2.37
0.7	2.25	2.23
0.8	2.16	2.12
0.9	2.10	2.04

**Fig. 5** Comparison of estimated  $n_{\text{equ}}$  by matching the phase boundaries (filled squares) and calculated  $n_{\text{equ}}$  using the expression of eqn (10) for linear-hyperbranched copolymers with different  $\tau$ ,  $\alpha = 1.6$  (red solid) for: (a)  $f_{\text{B}3} = f_{\text{B}}/4$ ; (b)  $f_{\text{B}3} = f_{\text{B}}/6$ .

smaller than the data points for  $\tau \gtrsim 0.5$ , then becomes larger than the data points for  $\tau \lesssim 0.5$ . Overall, the fitting curve with  $\alpha = 1.6$  is in good agreement with those data points.

Similarly, we estimate the values of  $n_{\text{equ}}$  by the matching approach for  $f_{\text{B}3} = f_{\text{B}}/6$  listed in Table 1. Using the expression in eqn (10) to fit these data points, we also obtain  $\alpha \approx 1.6$ . The fitting curve and the data points plotted in Fig. 5(b) show good agreement. These results demonstrate that  $n_{\text{equ}}$  of the linear-hyperbranched copolymer with varying architectures can be roughly estimated using the expression of eqn (10). Note that the linear-hyperbranched copolymer with  $f_{\text{B}3} = f_{\text{B}}/6$  and  $\tau = 0.5$  becomes the three-generation linear-dendrimer architecture (*i.e.*  $g = 3$ ) with equal B-blocks and its asymmetric effect on the spontaneous curvature can be roughly quantified by the  $n_{\text{equ}} \approx 2.5$  intermediate between those of  $\text{AB}_2$  and  $\text{AB}_3$  copolymers.

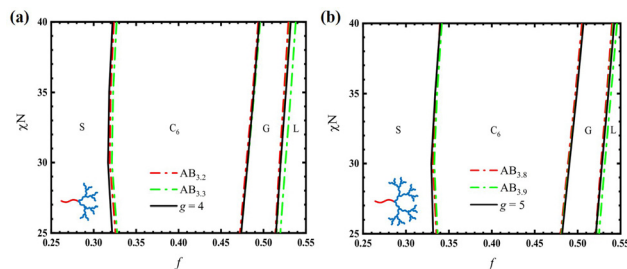
To understand how the asymmetric effect of the linear-dendrimer copolymer on the spontaneous curvature or the

**Table 2** List of  $f_{\text{B}}/f_{\text{B}}$  for the considered linear-hyperbranched copolymers or  $\text{AB}_n$ 

Copolymer	$f_{\text{B}1}/f_{\text{B}}$ (%)	$f_{\text{B}2}/f_{\text{B}}$ (%)	$f_{\text{B}3}/f_{\text{B}}$ (%)	$f_{\text{B}4}/f_{\text{B}}$ (%)
$\tau = 1/3$	16.7	8.3	25	—
$\tau = 2/3$	8.3	16.7	25	—
$\text{AB}_{2,4}$	4.6	4.6	45.4	45.4
$\text{AB}_{3,0}$	10.6	10.6	39.4	39.4
$\text{AB}_{3,2}$	12.5	12.5	37.5	37.5
$\text{AB}_{3,3}$	13.5	13.5	36.5	36.5
$\text{AB}_{3,8}$	19.2	19.2	30.8	30.8
$\text{AB}_{3,9}$	21.0	21.0	29.0	29.0

phase boundaries changes with increasing  $g$ , we directly estimate  $n_{\text{equ}}$  using the matching approach for  $g = 4$  and  $g = 5$ , respectively. In Fig. 6(a), we calculated the sphere/cylinder/gyroid/lamella boundaries of  $\text{AB}_4$  with unequal arms in the range of  $25 \leq \chi N \leq 40$  as well as those of the linear-dendrimer copolymer with  $g = 4$ . For  $\text{AB}_4$ , we consider two samples with  $n_{\text{equ}} = 3.20$  and  $n_{\text{equ}} = 3.30$ . The comparison of the phase boundaries suggests that the phase boundaries of  $\text{AB}_4$  with  $n_{\text{equ}} = 3.20$  are in good agreement with those of the linear-dendrimer copolymer with  $g = 4$ , and are noticeably better than those of  $\text{AB}_4$  with  $n_{\text{equ}} = 3.30$ . Accordingly, we quantify the asymmetric effect of the linear-dendrimer copolymer with  $g = 4$  to be  $n_{\text{equ}} \approx 3.20$ . Similarly, we estimate  $n_{\text{equ}} \approx 3.80$  for the linear-dendrimer copolymer with  $g = 5$ .

In Fig. 7(a), we plot the estimated  $n_{\text{equ}}$  of the different linear-dendrimer copolymers with respect to  $g$ . When  $g = 2$  increases to  $g = 3$ , the B-blocks at the outermost generation increase from 2 to 4, only raising  $n = 2$  to  $n_{\text{equ}} \approx 2.5$ . In other words, the asymmetric effect of the linear-dendrimer copolymer with  $g = 3$  is lower than that of  $\text{AB}_3$  with equal arms. When  $g = 3$  changes to  $g = 4$ , eight B-blocks are added at the outmost generation, while  $n_{\text{equ}} \approx 2.5$  increases to  $n_{\text{equ}} \approx 3.2$ . These results demonstrate that the addition of these B-blocks at the outer generation has less effect on the asymmetry. For the  $\text{AB}_n$  copolymer, the packing of B-blocks nearby the A/B interface is very crowded, so it forces the interface to bend toward the A-block. The curved interface generates more space for the multiple B-blocks, thus reducing their stretching degree. In contrast, as the generation of the linear-dendrimer copolymer increases, B-blocks are added to the outermost generation while keeping

**Fig. 6** Partial phase boundaries of: (a)  $\text{AB}_{3,2}$  (red dot-dashed lines),  $\text{AB}_{3,3}$  (green dot-dashed lines), and the linear-dendrimer copolymer with  $g = 4$  (solid lines); (b)  $\text{AB}_{3,8}$  (red dot-dashed lines),  $\text{AB}_{3,9}$  (green dot-dashed lines), and the linear-dendrimer copolymer with  $g = 5$  (solid lines). The length percentages of the B-blocks for all considered  $\text{AB}_n$  are listed in Table 2.

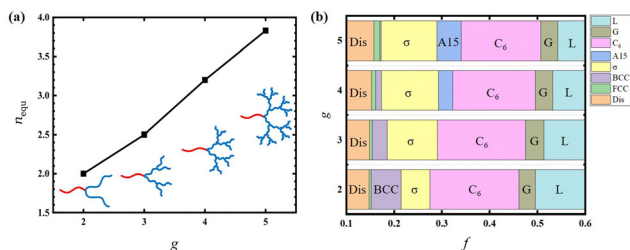


Fig. 7 (a) Variation of estimated  $n_{\text{equ}}$  for different linear-dendrimer copolymers with  $g = 2, 3, 4$  and  $5$ ; (b) comparison of the disorder/FCC/BCC/Frank–Kasper/ $C_6$ /G/L phase boundaries of these different linear-dendrimer copolymers at  $\chi N = 40$ .

the B-blocks directly joined with the single A-block unchanged. In particular, as these B-blocks move away from the A/B junction or the A/B curved interface, they can access expanding space and thus they have less effect on the curvature. Even for  $g = 5$  with sixteen B-blocks at the outermost generation, its asymmetric effect on the phase diagram is still lower than that of  $\text{AB}_4$  with equal arms because of  $n_{\text{equ}} \approx 3.8$ .

Previous works<sup>42,44,47,48,51</sup> have shown that the architectural asymmetry of the block copolymer is commonly encoded into its phase diagram, leading to an expansion of the spherical phase region on one side and a compression on the opposite side. In the widened spherical region, complex Frank–Kasper phases tend to appear. Our previous work<sup>51</sup> on asymmetric  $\text{AB}_n$  copolymers with unequal B-arms demonstrated that the emergence of Frank–Kasper phases could be quantitatively indicated by the value of  $n_{\text{equ}}$ . Specifically, the Frank–Kasper  $\sigma$ -phase appears when  $n_{\text{equ}} \gtrsim 1.5$ , while the another Frank–Kasper A15-phase starts to emerge for  $n_{\text{equ}} \gtrsim 2.5$ . To further confirm that such conclusions also hold for the linear-dendrimer copolymers, we calculated the disorder/FCC/BCC/Frank–Kasper/ $C_6$ /G/L phase boundaries for the linear-dendrimer copolymers with  $g = 2, 3, 4$ , and  $5$  at  $\chi N = 40$ , as shown in Fig. 7(b). In the phase sequence of  $g = 3$ , there is a wide region of  $\sigma$ -phase but no A15 phase region due to  $n_{\text{equ}} \approx 2.5$ . For  $g = 4$  with  $n_{\text{equ}} \approx 3.2 > 2.5$ , there exists a considerable region of A15-phase.

## 4 Conclusion

In summary, we have investigated the self-assembly behaviors of linear-hyperbranched copolymers using self-consistent field theory (SCFT). Firstly, we view the three-generation linear-hyperbranched copolymers as the derivatives of  $\text{AB}_n$  with equal or unequal B-arms. Different linear-hyperbranched copolymers are generated by moving two B-blocks along the arms of  $\text{AB}_2$ , and their equivalent arm numbers  $n_{\text{equ}}$  are estimated by comparing their phase boundaries with those of  $\text{AB}_n$  copolymers with unequal B-arms. The result of  $2 \leq n_{\text{equ}} \leq 4$  suggests that their asymmetric effect on the spontaneous curvature or the deflection of phase boundaries, which is intermediate between those of  $\text{AB}_2$  and  $\text{AB}_4$  copolymers, is dependent on the tethering distance from the A/B junction point.

Then we turn to study the asymmetric effect of the linear-dendrimer copolymers composed of linear A-block as the first

generation and equal B-block on the outer  $g - 1$  generations. Note that the linear-dendrimer copolymer with  $g = 2$  is  $\text{AB}_2$ . For  $g = 3, 4$  and  $5$ , the equivalent arm numbers are estimated as  $n_{\text{equ}} \approx 2.5, 3.2$  and  $3.8$ , respectively. The changing tendency of  $n_{\text{equ}}$  with  $g$  indicates that the addition of B-blocks at the outer generation has less effect on the spontaneous curvature because they are further from the A/B junction. The asymmetric effect of the linear-dendrimer copolymer quantified by the value of  $n_{\text{equ}}$  is confirmed by the changing trend of these spherical phase regions. Specifically, the phase sequence of  $g = 3$  contains Frank–Kasper  $\sigma$ -phase but no A15-phase because  $n_{\text{equ}} \approx 2.5$  is close to the critical value of  $n_{\text{equ}}$  for the emergence of A15. Since  $n_{\text{equ}}$  increases to about  $3.2$  for  $g = 4$ , a noticeable region of A15 appears in the phase sequence. Our work provides a comprehensive understanding of the asymmetric effect on the phase boundaries for linear-hyperbranched copolymers.

## Data availability

Isosurface plots and the corresponding parameters of the candidate ordered phases considered in the current study are available in the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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