

Scattering Function and Spinodal Transition of Linear and Nonlinear Block Copolymers Based on a Unified Molecular Model

Weichao Shi*

Key Laboratory of Functional Polymer Materials of Ministry of Education; Institute of Polymer Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

 Electronic Supplementary Information

Abstract This work uses a block copolymer architecture $[(A'B)_nA_2]_m$ to unify the scattering function and spinodal transition of typical AB-type block copolymers. The key roles of block number, junction points and asymmetry ratios of block length are (1) to determine the form factor of each block copolymer at the molecular scale; (2) to affect the entropy loss across the spinodal transition and may result in deflection of spinodal curves. The common features are validated in typical linear and nonlinear block copolymers, including AB diblock, asymmetric A'BA triblock, miktoarm stars of AB_n , A_nB_n , $(AB)_n$, $(A'B)_nA$, $A'BA_m$, and multi-graft combs of $(B_nA_2)_m$ and $[(A'B)_nA_2]_m$. The explicit scattering functions and form factors of various block copolymers can be directly applied in radiation experiments (*i.e.* neutron or X-ray scattering) to unravel the effect of molecular architecture in solution and microphase separation in disordered melt. The molecular model used in this study is also helpful to guide the chemical synthesis to explore more potentially interesting block copolymers.

Keywords Scattering function; Form factor; Spinodal transition; Molecular structure; Block copolymer

Citation: Shi, W. Scattering function and spinodal transition of linear and nonlinear block copolymers based on a unified molecular model. *Chinese J. Polym. Sci.* 2021, 39, 779–788.

INTRODUCTION

Pioneering experimental and theoretical work has led to significant progress in understanding the microphase separation of block copolymers in the past decades.^[1–3] The mean-field based theories provide a powerful tool to investigate the equilibrium phase structures.^[4] For the simple AB diblock copolymer, the phase diagram is well understood by three parameters: the total number of segments (N), the interaction parameter of the two components (χ), and the volume fraction (f_A). In an unlimited variety of AB-type block copolymers, molecular architecture has been realized to be an additional parameter to regulate their thermodynamics.^[5–9] Various nonlinear molecular architectures are created to enrich the category of block copolymers, such as miktoarm stars of homoblocks, miktoarm stars of diblocks, grafted combs and so on.^[10–17] These block copolymers are attracting intensive attention in fundamental research and broad interest in nanotechnologies, biomedical materials and thermoplastic elastomers.^[18–28]

The AB_n -type miktoarm star is one of the well-studied nonlinear block copolymers. The asymmetric block number at the junction point leads to asymmetric phase boundaries and new nanostructures, compared with an AB diblock copoly-

mer.^[5,6,16] The A_nB_n miktoarm stars of homoblocks and $(AB)_n$ miktoarm stars of diblocks have also been well exploited experimentally and theoretically.^[5,7,17] Matsen summarized the effect of architecture of such nonlinear block copolymers on phase diagrams almost one decade ago.^[9] New miktoarm block copolymers were purposely designed and synthesized in recent years. For example, an $(A'B)_3A$ miktoarm block copolymer, taking advantage of nonlinear architecture and bidispersed A and A' blocks, exhibits significantly asymmetric phase diagram and superior mechanical properties over conventional ABA triblock counterpart, which may serve as a new generation of thermoplastic elastomers.^[26–31] Li and Shi *et al.* have promptly expanded the two-component block copolymers with even more complicated architectures, including irregular stars and dendritic block copolymers.^[32–37] With the rapid progress on block copolymer studies, it is of great importance to demonstrate the effect of different architectures by one unified molecular model.

It is of great significance to combine the theoretical model explicitly with scattering techniques. Small-angle X-ray/neutron scattering is the most powerful tool to characterize the order-disorder transition (ODT) of block copolymers.^[38] The scattered pattern of an ordered nanostructure obeys scattering principles from crystal-like structures (such as body-centered cubic spheres, hexagonally packed cylinders, double gyroids and lamellae), while the scattering from solution or disordered melt requires more information of the detailed

* Corresponding author, E-mail: weichaoshi@nankai.edu.cn

Received November 29, 2020; Accepted December 30, 2020; Published online February 10, 2021

molecular architecture. The scattering function for diblock copolymers was first developed by Leibler in the context of mean field theory with random phase approximation.^[2] The scattering function is directly related to the scattering curves and is quantitatively used to calculate interaction parameters. The theory was subsequently applied to AB_n , A_nB_n and $(AB)_n$ miktoarm stars.^[5] An explicit formula of scattering function is certainly an essential link between theories and experiments in disordered melts and in polymer solutions.^[17] But the scattering functions for more complicated block copolymers are still missing. Establishing a unified molecular model would be helpful to grasp the common features of those well-understood and the newly created block copolymers in scattering experiments.

Targeting the above two goals, a unified molecular model, $[(A'B)_nA_2]_m$, is proposed to study its phase behavior in disordered state, where A and A' blocks are of the same chemical constitution but different lengths; n and m are the numbers of A'B block and the repeat number of $(A'B)_nA_2$, respectively. Specific block copolymer architectures can be easily derived from this molecular design (Fig. 1), including conventional linear block copolymers, such as diblock AB, symmetric triblock ABA, and asymmetric triblock ABA'; nonlinear miktoarm stars of homoblocks, AB_n , A_nB_n , A_mB_n ; stars of diblock arms $(AB)_n$; stars of mixed homo/diblock arms $(A'B)_nA_m$; and comb-like block copolymers $(B_nA_2)_m$ and $[(A'B)_nA_2]_m$. Very simple mathematics within the framework of Leibler's theory is employed to demonstrate the general roles of the arm

number, the junction point and the asymmetry of block length in different molecular architectures. This research provides a simple protocol to complement scattering experiments and to guide the chemical synthesis to potentially interesting block copolymers.

THEORETICAL MODEL

General Considerations

In the one-phase region, the free energy associated with composition variation is written as,

$$\delta G = \left(\frac{\partial G}{\partial \phi} \right) \langle \delta \phi_j \rangle + \frac{1}{2} \left(\frac{\partial^2 G}{\partial \phi^2} \right) \langle \delta \phi_j \delta \phi_k \rangle + \dots \quad (1)$$

where the $\langle \rangle$ denotes a thermal average. The first term on the right is obviously zero and the higher-order terms are neglected. The second term is written as,

$$\langle \delta \phi_j \delta \phi_k \rangle = kT \left(\frac{\partial^2 G}{\partial \phi^2} \right)^{-1} \quad (2)$$

From classic thermodynamics, spontaneous phase separation occurs when $\frac{\partial^2 G}{\partial \phi^2} < 0$. The composition amplitude diverges at the spinodal point when $\frac{\partial^2 G}{\partial \phi^2} = 0$.

In real space, the composition correlation at j and k is reflected by the structure factor $S(\mathbf{r}_{jk})$,

$$\langle \delta \phi_j \delta \phi_k \rangle = S(\mathbf{r}_{jk}) \quad (3)$$

The structure factor in reciprocal space is obtained by the Fourier transform,

$$S(q) \cong \int d\mathbf{r}_{jk} \exp(iq \cdot \mathbf{r}_{jk}) S(\mathbf{r}_{jk}) \quad (4)$$

The prefactor is dropped on the right for simplicity. The structure factor can be directly measured by scattering experiment,

$$I(q) = (I_A - I_B)^2 S(q) \quad (5)$$

where $I(q)$ is the scattered intensity and the term before $S(q)$ denotes the scattering contrast. In the small angle X-ray or neutron scattering, I_A and I_B are scattering length densities of each component. The q is related to the scattered angle θ and the wavelength of the beam λ in scattering experiment by the relation $q = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$.

The structure factor of a Gaussian chain is defined as the integrated probability of all N segments to find the j^{th} segment at point $\mathbf{r}_j$ and the k^{th} segment at point $\mathbf{r}_k$,

$$S(q) = \frac{1}{N} \int_0^N \int_0^N \langle \exp(iq \cdot \mathbf{r}_{jk}) \rangle djdk \quad (6)$$

The integration leads to the well-known form of the Debye function,

$$S(q) = \frac{1}{N} \frac{2}{\left(\frac{q^2 b^2}{6} \right)^2} \left[\frac{q^2 b^2}{6} N + \exp \left(-\frac{q^2 b^2}{6} N \right) - 1 \right] = \frac{1}{N} g(N) \quad (7)$$

where b is the segment length. Notice that the Debye function $g(N)$ is defined slightly different from a conventional form. If x is used to take place of $q^2 b^2 / 6$, the Debye function is rewritten as,

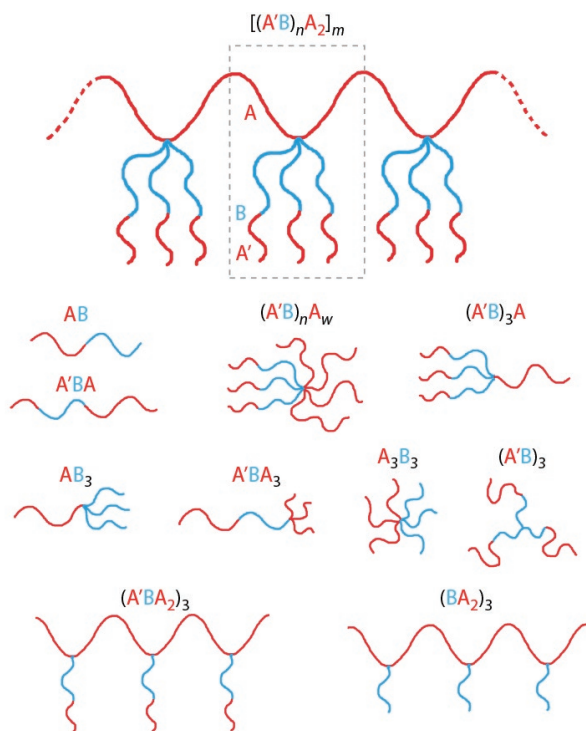


Fig. 1 The unified molecular model $[(A'B)_nA_2]_m$ and its derivatives, including a miktoarm model $(A'B)_nA_w$, AB diblocks, A'BA linear triblocks, miktoarm stars of homoblocks AB_n or A_nB_n , miktoarm stars of diblocks $(A'B)_n$, miktoarm stars of homo/diblock arms $(A'B)_nA$ or $A'BA_w$, multi-graft combs $(BA_2)_m$ and $(A'BA_2)_m$. Specific block copolymer architectures with $n=m=w=3$ are drawn for illustration.

$$g(N) = \frac{2}{\chi^2} [\chi N + \exp(-\chi N) - 1] \quad (8)$$

The scattering function of a two-component block copolymer was first developed by Leibler,^[2]

$$S(q) = \frac{W}{S^t - 2\chi W} \quad (9)$$

$$S^t = S_{AA}^t + S_{BB}^t + 2S_{AB}^t \quad (10)$$

$$W = S_{AA}^t S_{BB}^t - (S_{AB}^t)^2 \quad (11)$$

The interaction between the two chemical species is denoted by χ . This set of equations was originally obtained based on mean-field theory with random phase approximation (RPA) to describe the microphase separation of AB diblock copolymers in weak segregation regime. Thermal fluctuation effect is ignored in the theory. More generally, similar equations can be derived for all binary systems, i.e. diblock copolymers, or binary polymer blends.^[39]

To set a unified molecular architecture, a special miktoarm structure $(A'B)_n A_2$ is taken as the repeating unit in a long comb-like block copolymer, $[(A'B)_n A_2]_m$ (Fig. 1). The two A blocks are covalently linked to form the backbone, and the $(A'B)_n$ are pendent blocks at a junction point. The A' and A blocks are constituted of the same chemical species, and their block lengths are N_1 and N_3 , respectively. The B block has N_2 segments. The total segment number in the molecule is thus

$$N_t = m(nN_1 + nN_2 + 2N_3) \quad (12)$$

Suppose A and B have the same segment length b and the same segment volume, then the volume fraction of A is

$$f_A = \frac{nN_1 + 2N_3}{nN_1 + nN_2 + 2N_3} \quad (13)$$

The asymmetry ratio is defined as the fraction of an A block in the A'+A in one A'BA strand:

$$\tau = \frac{N_3}{N_1 + N_3} \quad (14)$$

The pair correlations of AA, BB and AB are:

$$S_{AA}^t = S_{AA} + nmS_{A'A'}^{ij} + n(n-1) \sum_{i \neq j}^m S_{A'A'}^{ij} + n^2 \sum_{i=1}^m \sum_{j=1}^m S_{A'A'}^{ij} + 2n \sum_{i=1}^m S_{AA'}^i \quad (15)$$

$$S_{BB}^t = nmS_{BB}^{ij} + n(n-1) \sum_{i \neq j}^m S_{BB}^{ij} + n^2 \sum_{i=1}^m \sum_{j=1}^m S_{BB}^{ij} \quad (16)$$

$$S_{AB}^t = nmS_{A'B}^{ij} + n(n-1) \sum_{i \neq j}^m S_{A'B}^{ij} + n^2 \sum_{i=1}^m \sum_{j=1}^m S_{A'B}^{ij} + n \sum_{i=1}^m S_{AB}^i \quad (17)$$

One key assumption of RPA is that chains remain nearly ideal on the scale of polymer strands in a dense polymer system. Accordingly, the correlation of any two points in a linear strand in a complicated block copolymer architecture simply follows the Debye function. The correlation function of two A segments in the backbone is thus

$$S_{AA} = N_t^{-1} g(2mN_3) \quad (18)$$

The correlation function of two A' segments in the same block is

$$S_{A'A'}^{ij} = N_t^{-1} g(N_1) \quad (19)$$

The correlation function of an A' segment tethered at the i^{th} junction point and another A' segment at the j^{th} junction

point is

$$S_{A'A'}^{ij} = \frac{1}{2} [S_{A'B(AA)}^0|_{i-j}|_{BA'} - S_{A'B(AA)}^0|_{i-j}|_B - S_{B(AA)}^0|_{i-j}|_{BA'} + S_{B(AA)}^0|_{i-j}|_B] \quad (20)$$

$$\text{where } S_{A'B(AA)}^0|_{i-j}|_{BA'} = N_t^{-1} g(2N_1 + 2N_2 + 2|i-j|N_3) \quad (21)$$

$$S_{A'B(AA)}^0|_{i-j}|_B = S_{B(AA)}^0|_{i-j}|_{BA'} = N_t^{-1} g(N_1 + 2N_2 + 2|i-j|N_3) \quad (22)$$

$$S_{B(AA)}^0|_{i-j}|_B = N_t^{-1} g(2N_2 + 2|i-j|N_3) \quad (23)$$

The correlation function of A and A' segments at the i^{th} junction point is

$$S_{AA'}^i = \frac{1}{2} [S_{A_{2i-1}BA'}^0 - S_{A_{2i-1}B}^0 - S_{BA'}^0 + S_{BB}^{ii}] + \frac{1}{2} [S_{A_{2m-2i+1}BA'}^0 - S_{A_{2m-2i+1}B}^0 - S_{BA'}^0 + S_{BB}^{ii}] \quad (24)$$

$$\text{where } S_{A_{2i-1}BA'}^0 = N_t^{-1} g(N_1 + N_2 + 2iN_3 - N_3) \quad (25)$$

$$S_{A_{2i-1}B}^0 = N_t^{-1} g(2iN_3 - N_3 + N_2) \quad (26)$$

$$S_{BA'}^0 = N_t^{-1} g(N_1 + N_2) \quad (27)$$

$$S_{A_{2m-2i+1}BA'}^0 = N_t^{-1} g(N_1 + N_2 + 2mN_3 - 2iN_3 + N_3) \quad (28)$$

Similarly, the correlation function of two B segments in the same block is

$$S_{BB}^{ii} = N_t^{-1} g(N_2) \quad (29)$$

The correlation of a B segment in the i^{th} junction point and a B segment in the j^{th} junction point is

$$S_{BB}^{ij} = \frac{1}{2} [S_{B(AA)}^0|_{i-j}|_B - S_{B(AA)}^0|_{i-j}|_{BA'} - S_{(AA)}^0|_{i-j}|_B + S_{(AA)}^0|_{i-j}|_{BA'}] \quad (30)$$

$$\text{where } S_{B(AA)}^0|_{i-j}|_B = S_{(AA)}^0|_{i-j}|_{BA'} = N_t^{-1} g(N_2 + 2|i-j|N_3) \quad (31)$$

$$S_{(AA)}^0|_{i-j}|_{BA'} = N_t^{-1} g(2|i-j|N_3) \quad (32)$$

The correlation function of an A' and a B segment in the same block is

$$S_{A'B}^{ij} = \frac{1}{2} [S_{A'B}^0 - S_{A'A'}^{ij} - S_{BB}^{ij}] \quad (33)$$

The correlation function of an A' segment in the i^{th} junction point and a B segment in the j^{th} junction point is

$$S_{A'B}^{ij} = \frac{1}{2} [S_{A'B(AA)}^0|_{i-j}|_B - S_{A'B(AA)}^0|_{i-j}|_{BA'} - S_{B(AA)}^0|_{i-j}|_B + S_{B(AA)}^0|_{i-j}|_{BA'}] \quad (34)$$

The correlation function of an A segment and a B segment at the i^{th} junction point is

$$S_{AB}^i = \frac{1}{2} [S_{A_{2i-1}B}^0 - S_{A_{2i-1}}^{ii} - S_{BB}^{ii}] + \frac{1}{2} [S_{A_{2m-2i+1}B}^0 - S_{A_{2m-2i+1}}^{ii} - S_{BB}^{ii}] \quad (35)$$

$$\text{where } S_{A_{2i-1}B}^0 = N_t^{-1} g(2iN_3 - N_3 + N_2) \quad (36)$$

$$S_{A_{2i-1}}^{ii} = N_t^{-1} g(2iN_3 - N_3) \quad (37)$$

$$S_{A_{2m-2i+1}B}^0 = N_t^{-1} g(N_2 + 2mN_3 - 2iN_3 + N_3) \quad (38)$$

$$S_{A_{2m-2i+1}}^{ii} = N_t^{-1} g(2mN_3 - 2iN_3 + N_3) \quad (39)$$

The repeat unit $(A'B)_n A_2$ in this comb-like block copolymer $[(A'B)_n A_2]_m$ can be slightly modified to get a miktoarm star of $(A'B)_n A_w$ (Fig. 1), which consist of n arms of A'B diblock and w arms of A block. The scattering function of $(A'B)_n A_w$ is given in

the electronic supplementary information (ESI, Part A). By setting appropriate values of n , m , w , N_1 , N_2 and N_3 , the molecular model proposed above can be simplified to specific linear and nonlinear block copolymers, including AB diblocks, linear A'BA triblocks, miktoarm star of diblocks (A'B) $_n$, miktoarm star of homoblocks AB $_n$ or A $_w$ B $_n$, miktoarm stars of homo/diblock arms (A'B) $_n$ A or A'BA $_w$, multi-graft combs (BA $_2$) $_m$ and (A'BA $_2$) $_m$. These special block copolymer architectures are illustrated in Fig. 1 with $n=m=w=3$. In ESI (Part B), an example is shown to reflect how to simplify the unified molecular model [(A'B) $_n$ A] $_m$ to the (BA $_2$) $_2$ comb-like block copolymer. In experiment, the detailed values of n , m , w , N_1 , N_2 and N_3 can be controlled by living polymerization methods.^[40] The above set of functions can thus be applied to synthetic block copolymers directly.

RESULTS AND DISCUSSION

Molecular Architectures and Form Factors

When a block copolymer is dissolved in a dilute θ solution (no assembled micelles), the scattered intensity is contributed by each individual polymer. In disordered melt, a block

copolymer maintains a Gaussian nature as modeled in the Leibler's theory, irrespective of interaction between distinct monomer pairs. The architecture of a specific block copolymer is distinguished by the form factor $F(q)$, which is related to its structure factor by

$$F(q) = \frac{S^t(q)}{S^t(0)} = \frac{1}{N_t} S^t(q) \quad (40)$$

The form factors of A $_n$ B $_n$ block copolymers are shown in Fig. 2(a). The form factors of all A $_n$ B $_n$ block copolymers converge to 1 at $qR_g < 1$. At $qR_g > 1$, the AB diblock copolymer exhibits a characteristic power index $F(q) \sim q^{-2}$, which represents the topology of a linear Gaussian chain. Increasing the number of arms in A $_n$ B $_n$, the segments become concentrated near the junction point and look like a sphere when n is very large. This structural feature indicates that the form factor approaches a power index of a compact sphere $F(q) \sim q^{-4}$ at $qR_g \sim 1$, while still behaves as a Gaussian chain $F(q) \sim q^{-2}$ at $qR_g \gg 1$. Increasing the arm number shifts a coil topology to a compact 3D architecture. This effect also applies to the form factors of other miktoarm stars (AB) $_n$ and multigraft comb-like block copolymers (B $_n$ A $_2$) $_m$ (Part C in ESI).

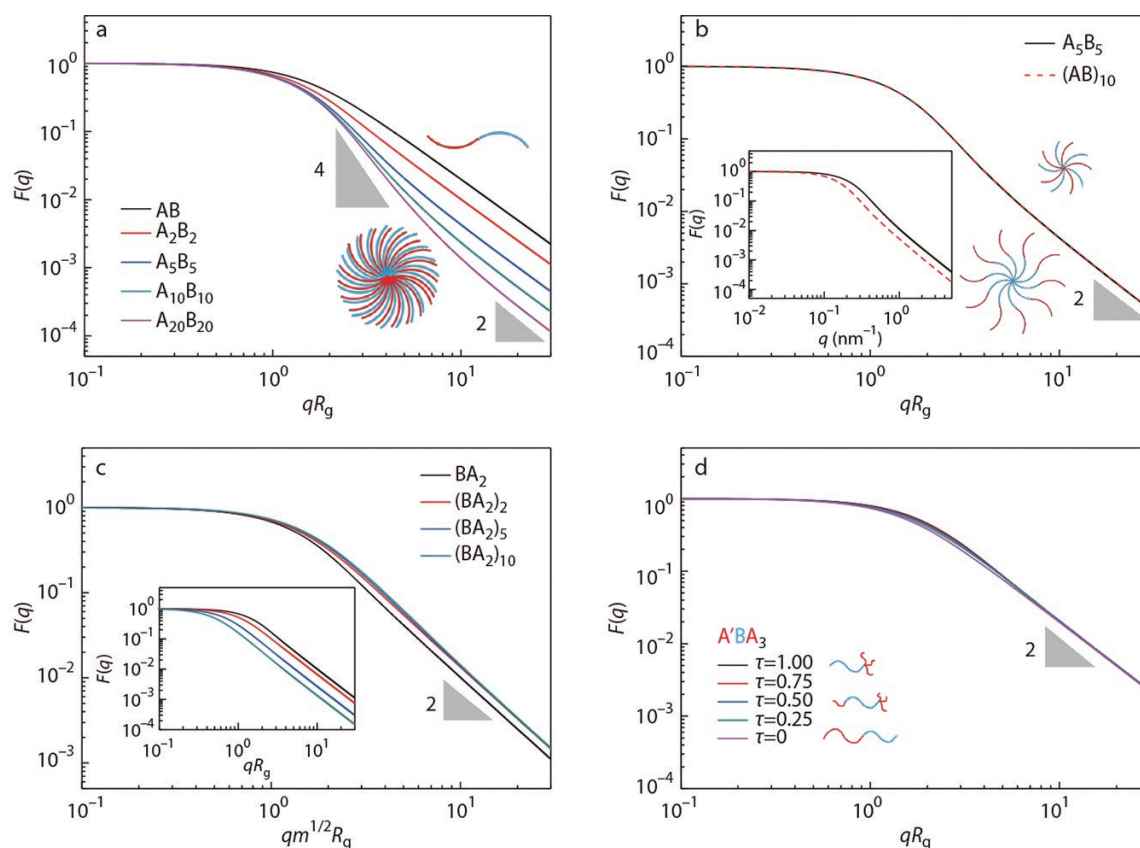


Fig. 2 Form factors of block copolymers. The form factors of A $_n$ B $_n$ block copolymers are shown in (a). The form factors of an A $_5$ B $_5$ and an (AB) $_{10}$ block copolymer are shown by a $F(q)$ - qR_g plot in (b) and a $F(q)$ - q plot in the inset. The form factors of (BA $_2$) $_m$ block copolymers are shown by a $F(q)$ - $qm^{1/2}R_g$ plot in (c) and a $F(q)$ - qR_g plot in the inset. The block lengths of $N_A=N_B=500$ and $b=0.5$ nm are used in (a–c). The radius of gyration of one AB strand, $R_g=[(N_A+N_B)/6]^{1/2}b$, is used in (b) to rescale the form factors. The radius of gyration of one A strand, $R_g=(N_A/6)^{1/2}b$, is used in (c) to rescale the form factors. The total block lengths of 3000 and $b=0.5$ nm are used in (a–c). The form factors of A'BA $_3$ block copolymers are shown in (d). The $N_B=1500$ and the total segment number of all A segments is 1500. The R_g at $\tau=0$ (diblock) is used to rescale the form factors.

The $(AB)_n$ block copolymers generally have different form factors from A_nB_n . But it should be noted that the topological features of symmetric A_nB_n and $(AB)_{2n}$ are very similar and scalable. An A_5B_5 and an $(AB)_{10}$ miktoarm are used for illustration. Their form factors are obviously different in a $F(q)$ to q plot (inset in Fig. 2b). In the $(AB)_{10}$ miktoarm, the B segments are rich in the core while the A segments are rich in the shell. So, the A-A, B-B and A-B correlations in the $(AB)_{10}$ miktoarm are very different from those in A_5B_5 (Part D in ESI). But the form factors of $(AB)_{10}$ and A_5B_5 fall onto a normalized curve (Fig. 2b), if the radius of gyration of one AB diblock ($R_g = [(N_A + N_B)/6]^{1/2}b$) is used to rescale the form factors. This indicates that the form factors are scalable when block copolymers share similar topological feature.

In the multigraft comb-like block copolymers $(BA_2)_m$, each unit is a Y-shape BA_2 miktoarm. The $F(q)$ decreases significantly with the increase of m at $qR_g > 1$ (inset in Fig. 2c), while the topological power index of a Gaussian chain $F(q) \sim q^{-2}$ is well maintained. Accordingly, the form factors could be further rescaled by the repeat number $qm^{1/2}R_g$, where R_g is the radius gyration of one A strand in the backbone. In Fig. 2(c), the form factors of $(BA_2)_2$, $(BA_2)_5$ and $(BA_2)_{10}$ almost fall onto a normalized curve in the whole q range except very slight discrepancy at $qm^{1/2}R_g \sim 1$. In comparison, the form factor of BA_2 exhibits significant discrepancy at $qm^{1/2}R_g > 1$. The discrepancy indicates that the effect of chemical connectivity of BA_2 is significant when m increases from 1 to 2, but becomes insignificant when m exceeds 2.

The molecular model in this study can be extended to other complicated block copolymers. An example of an $A'BA_3$ miktoarm with different asymmetry ratios (τ , Eq. 14) is shown in Fig. 2(d). Variation of τ affects the form factor slightly at $qR_g \sim 1$, but does not alter the topological feature. After examination of various block copolymers, we conclude that the form factors of all molecular architectures converge to 1 at $qR_g \ll 1$ and the topological feature remains Gaussian at $qR_g \gg 1$. The effect of molecular architecture is significant at $qR_g \sim 1$, and is correlated with the number of arms, the junctions and the ratio of block length.

Molecular Architectures and Spinodal Transition

When block copolymers are considered in disordered melt, concentration inhomogeneity exists which grows stronger as the system approaches the spinodal point and eventually develops into ordered nanostructures. The dominant mode of concentration fluctuations is revealed by a peak in the scattering curve at a wavevector q_m . At the spinodal point, the scattered intensity diverges at q_m . In the calculation, $S(q_m)^{-1} = 0$ is used to define the spinodal point. The detailed method is explained in ESI (Part B). The correlation of molecular architecture and the spinodal boundary is investigated below.

The A_nB_n and $(BA)_n$ star block copolymers are well studied architectures in literature and are reproduced here for comparison.^[5,36] The A_nB_n miktoarms share one junction point (J1) in the middle of AB and exhibit symmetric spinodal boundaries (Figs. 3a and 3b). As n increases, the boundaries shift to lower segregation strengths. All the spinodal lines share a critical point at $f = 0.5$ and $\chi(N_A + N_B) = 10.5$. The $(BA)_n$ molecules share one junction point (J2) at the end of B blocks and exhibit

asymmetric spinodal boundaries (Figs. 3a and 3c). As n increases, the boundaries shift to lower segregation strengths at small f_A region. At high f_A region, the boundaries are less dependent of n and approach the spinodal boundary of the AB diblock copolymer. The $(B_2A_2)_n$ combs contain both J1 and J2 junctions, and their spinodal boundaries are slightly asymmetric (Fig. 3d). Increasing the repeating units results in slight drop of the spinodal boundaries at small f_A region. The lowering of spinodal boundaries indicates the microphase separation occurs at weaker segregation strengths.

As demonstrated in Fig. 3(a), A_4B_4 , $(BA)_4$ and $(B_2A_2)_2$ have the same number of A and B blocks, but their blocks are linked with different junctions, whose effect is significant as compared in Fig. 3(e). The spinodal line of $(B_2A_2)_2$ stays very close to A_4B_4 at low f_A region and locates between A_4B_4 and $(BA)_4$ at high f_A region, which indicates that the connection of two A blocks in $(B_2A_2)_2$ by one J2 junction plays trivial effect at small f_A , compared with the J2 junction in $(BA)_4$; while J1 junction in $(B_2A_2)_2$ takes effect at high f_A , but is less significant than the role of J1 in A_4B_4 .

The BA_2 (or AB_2) miktoarm is a typical example that the number of A and B blocks is unequal at J1. The spinodal boundary of BA_2 is slightly asymmetric (Figs. 4a and 4b). Combination of more BA_2 at J1 ($(B_nA_{2n})_n$) also shifts the spinodal boundaries to lower segregation strengths as n increases. Notice that all curves pass a special point at $f_A = 0.67$ ($\chi N = 17.9$), which indicates that the structure factor is independent of n at this specific point. At $f_A = 0.67$, each A/B arm has identical length. Thus, the junction point applies equal constraint to each arm. The junction constraint is significant below that point, while the effect is less significant above. Chemically linking BA_2 in series by the end of A block (J2), that is the comb-like block architecture $(BA_2)_n$, results in slight drop of the spinodal boundaries at small f_A region (Fig. 4c). The role of J2 is trivial at large f_A region.

From the above results, we may conclude that: (1) increasing the number of arms facilitates microphase separation; (2) since the J1 applies equal constraints to nearby blocks, anchoring an equal number of A and B blocks at J1 leads to symmetric decrease of spinodal boundary, while an unequal block number results in asymmetric effect; (3) the J2 applies constraint only to A blocks and thus leads to asymmetric spinodal boundaries with pronounced decrease at small f_A region. The asymmetry of block length is a bidispersity effect and shows an additional parameter that determines the microphase separation behavior.^[41] The linear A'BA, miktoarm stars of $(A'B)_nA$ and $A'BA_n$, and comb-like $(A'BA_2)_n$ are discussed in details below.

For the linear block copolymer A'BA (Part E in ESI), we can imagine that the structure reduces to an AB or A'B diblock copolymer at $\tau = 1$ or $\tau = 0$; it returns to a symmetric triblock copolymer ABA at $\tau = 0.5$. Thus, the spinodal boundaries shift upward from a symmetric curve of AB at a lower χN_t to asymmetric curves of A'BA at higher χN_t at $0 < \tau < 0.5$.^[42,43] The spinodal lines at $\tau = 0.5 \pm x$ ($0 \leq x \leq 0.5$) completely overlap.

For the miktoarm star $(A'B)_2A$ (Figs. 5a and 5d), the structure recedes to an AB_2 type block copolymer at $\tau = 1$; it returns to a linear triblock copolymer A'BBA' (equivalent to ABA) at $\tau = 0$. Increasing the length of two A' blocks in an $(A'B)_2A$ block

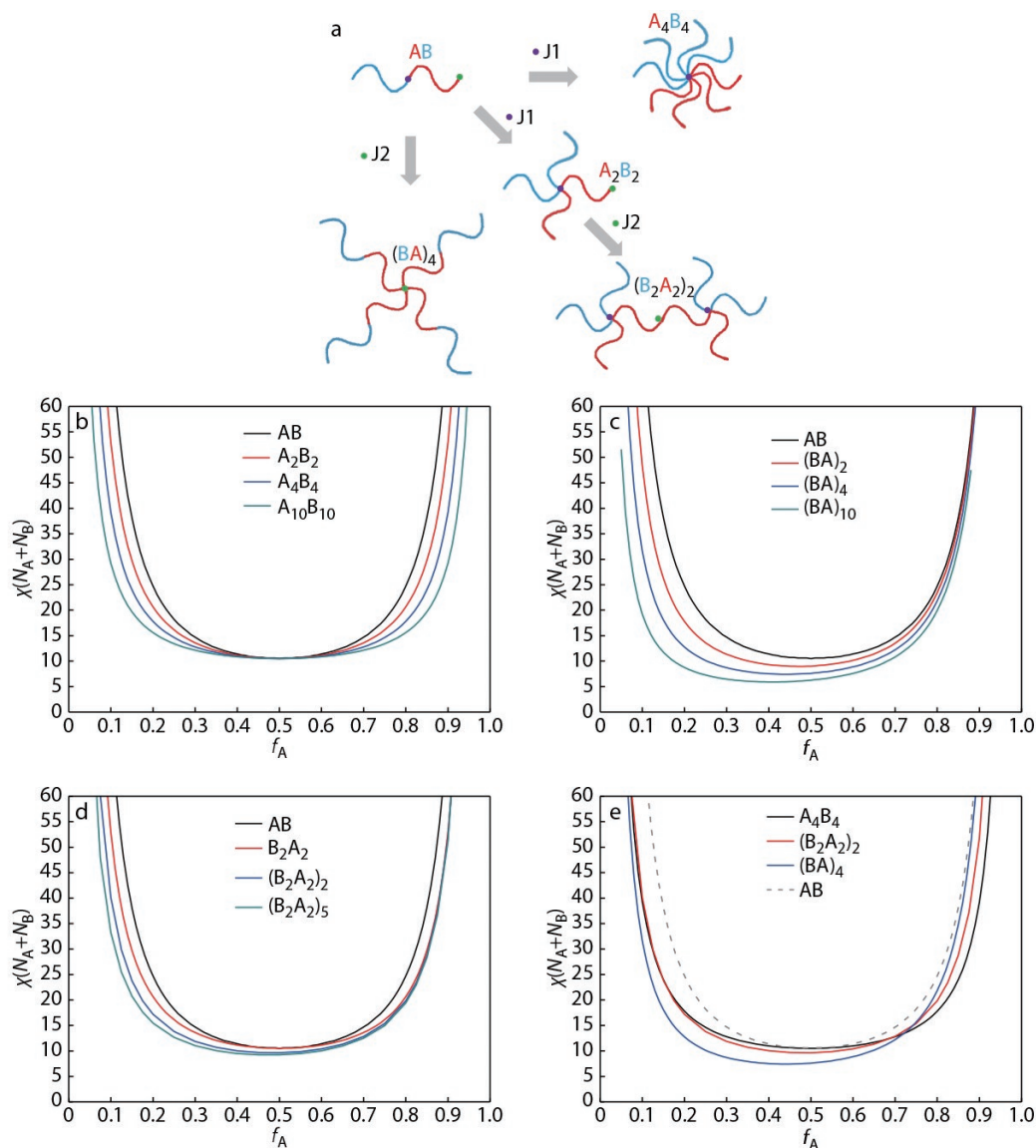


Fig. 3 Molecular architectures of A_4B_4 , $(BA)_4$ and $(B_2A_2)_2$ (a); Spinodal boundaries of A_nB_n (b), $(BA)_n$ (c) and $(B_2A_2)_n$ (d); Comparison of spinodal boundaries of AB, A_4B_4 , $(BA)_4$ and $(B_2A_2)_2$ (e).

copolymer leads to significant increase of spinodal boundaries until $\tau=0.6$; while decreasing the length of the A block relative to A' results in mild decrease of the spinodal boundaries for $\tau<0.6$. Notice that the spinodal line of ABA is higher than that of AB₂.

For the miktoarm star A'BA₂ (Figs. 5b and 5e), the structure reduces to an AB₂ type block copolymer at $\tau=1$ and returns to an A'B diblock copolymer at $\tau=0$. Increasing the length of the A' block in the A'BA₂ block copolymer leads to continuous increase of the spinodal boundaries from $\tau=1$ to $\tau=0.4$, while increasing A' block length at $\tau<0.4$ lowers the spinodal boundaries. Here, it should be noticed that the spinodal line of A'B is lower than that of BA₂.

The (A'BA₂)₅ molecular architecture connects comb-like and miktoarm star block copolymers by varying asymmetry ratios (Figs. 5c and 5f). The structure is a typical comb-like block copolymer (BA₂)₅ at $\tau=1$, where A is the backbone with

5 grafted B blocks; it returns to a miktoarm star block copolymer (A'B)₅ at $\tau=0$. Increasing the length of the A' block in the grafted A'B blocks leads to mild increase of the spinodal boundaries from $\tau=1$ to $\tau=0.2$; while decreasing the lengths of two A blocks in the backbone (higher graft density) results in significant asymmetry and decrease of the spinodal boundaries for $\tau<0.2$.

To further reveal the effects of the asymmetry ratio and the number of arms, the spinodal curve of each block copolymer is plotted against asymmetry ratio at a fixed composition $f_A=0.5$. The contour of the A'BA block copolymer is symmetric against $\tau=0.5$ (Fig. 5g). Increase in the number of arms of (A'B)_nA leads to significant increase of the spinodal boundary and deflection of the upper point to larger τ . The spinodal points of the AB_n miktoarm block copolymers at $\tau=1$ are lower than those of (A'B)_n at $\tau=0$. Increase in the number of arms of A'BA_m (Fig. 5h), in contrast, does not increase the spinodal

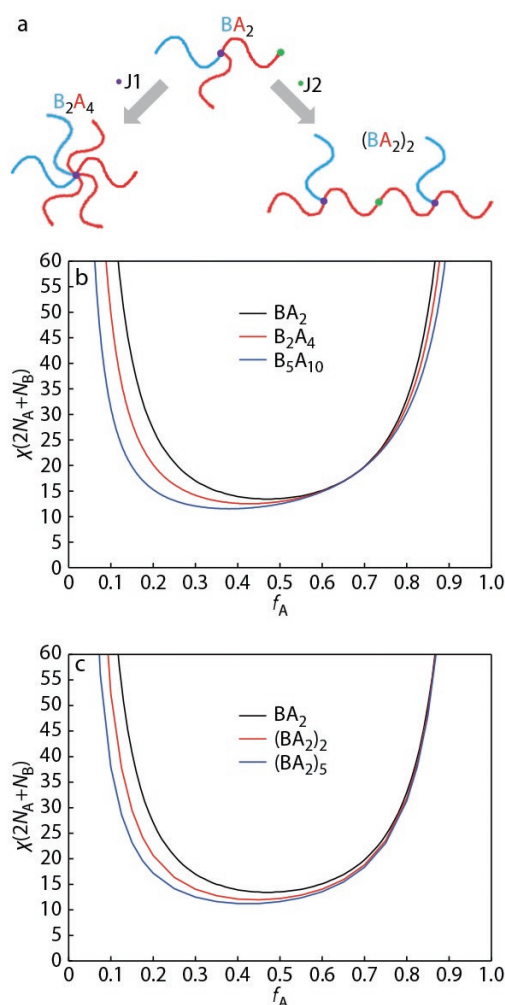


Fig. 4 Molecular architectures of BA₂, B₂A₄ and (BA₂)₂ (a); Spinodal boundaries of B_nA_{2n} (b), and (BA₂)_n (c).

boundary much, but significantly deflects the maximum to lower τ . All molecular structures recover to A'B at $\tau=0$, and its spinodal point is slightly lower than that of BA_n at $\tau=1$. Increase in the repeat number of the comb-like structure (A'BA₂)_m (Fig. 5i), however, decreases spinodal boundaries slightly and deflects the maximum to lower τ . It is interesting to find that all curves share a point at $\tau=0.17$. This indicates that the effect is independent of m when the length A' block is identical to the length of the two neighboring graft points. The spinodal points of an A'B unit in (A'B)_n at $\tau=0$ is lower than that of an BA₂ unit in (BA₂)_m at $\tau=1$.

Molecular Architectures and Entropy Loss

From the above results, the molecular architecture of an AB-type block copolymer generally refers to three key factors: the number of blocks, the junction point, and the block length. Each factor is closely correlated with the entropy change across the spinodal transition. The total entropy change of a block copolymer can be generally written as,

$$\Delta S = \Delta S_A + \Delta S_B + \Delta S_J \quad (41)$$

where ΔS_A , ΔS_B , ΔS_J are the entropy losses of A block, B block and junction point, respectively. Just across the spinodal line,

the translational entropy loss is substantial while the conformational entropy loss is negligible. Thus, the spinodal point can be view as the balance that the drop of repulsive interaction counteracts the translational entropy loss. Anchoring a block of N segments to a flat interface results in a translational entropy loss of $k\ln\sqrt{N}$.^[5] Suppose each junction point occupies a volume of v in the total volume V , the translational entropy loss of a junction point is $k\ln\frac{V}{v}$, where $v=V$ at the critical point and $v<V$ otherwise.

For the AB_n type miktoarm block copolymer, increasing number of arms (n) increases the entropy loss of the B blocks by $\frac{nk}{2}\ln N_B$, while the entropy loss of the A block and the junction point does not change. Thus, larger segregation strengths (large χN_t values) are required to counteract the entropy effect and initiate spinodal transition. Similarly, for the A_nB_n type miktoarm block copolymers, the total entropy loss of the junction point does not change, while that of the A and B blocks increases with n by $\frac{nk}{2}\ln(N_A N_B)$. The normalized entropy loss for each AB diblock in A_nB_n is then $\frac{k}{2}\ln(N_A N_B) + \frac{k}{n}\ln\frac{V}{v}$. For the A_nB_n block copolymers with fixed N_A and N_B , the entropy loss of each block is independent of n (the first term), but the entropy of junction decreases with n (the second term). Especial concern should be taken at $f_A=0.5$, where the block copolymer crosses the critical point with $v=V$. Accordingly, the normalized spinodal boundary of $\chi(N_A+N_B)$ is symmetric, independent of n at $f_A=0.5$ and decreases with n otherwise (Fig. 3b).

In (BA)_n miktoarm stars, there are two types of junction points, J1 and J2. The total entropy loss of the A and B blocks increases with n by $\frac{nk}{2}\ln(N_A N_B)$ and that of the J1 is $nk\ln\frac{V}{v}$. The J2 occupies a small volume v' in the A phase, which has a total volume of Vf_A . Thus, the total entropy loss of J2 is $k\ln\frac{Vf_A}{v'}$. The normalized entropy loss for each AB diblock in (BA)_n miktoarm star is $\frac{k}{2}\ln(N_A N_B) + k\ln\frac{V}{v} + \frac{k}{n}\ln\frac{Vf_A}{v'}$. The normalized entropies by A block, B block and J1 are independent of n , while the entropy of J2 decreases with n . Notice that the entropy also decreases with f_A . So the normalized spinodal boundary of $\chi(N_A+N_B)$ is asymmetric, drops downward at small f_A and decreases with the increase of the arm number n (Fig. 3c).

The (BA₂)_m comb-like block copolymers contain m junctions of J1 and $(m-1)$ junctions of J2 ($m\geq 2$). The repeated growth of BA₂ only affects the entropy of J2. The first J2 can be freely placed in the volume of Vf_A , while the other J2 points are subsequently correlated in a nearby volume of V_A that is accessible by one A block. V_A scales to $\sim R_{gA}^3$ and is much smaller than Vf_A . The normalized entropy loss of each BA₂ unit is therefore $\frac{k}{m}\ln\frac{Vf_A}{v'} + \frac{(m-2)k}{m}\ln\frac{V_A}{v'}$, which is dominated by the first term, decreases with m and increases with f_A . Thus, the spinodal curves of $\chi(2N_A+N_B)$ drops downward with the repeat number m , and are more significant at small f_A (Fig. 4c).

The effect of the asymmetry ratio of block length can be realized by a similar approach. For the A'BA triblock copoly-

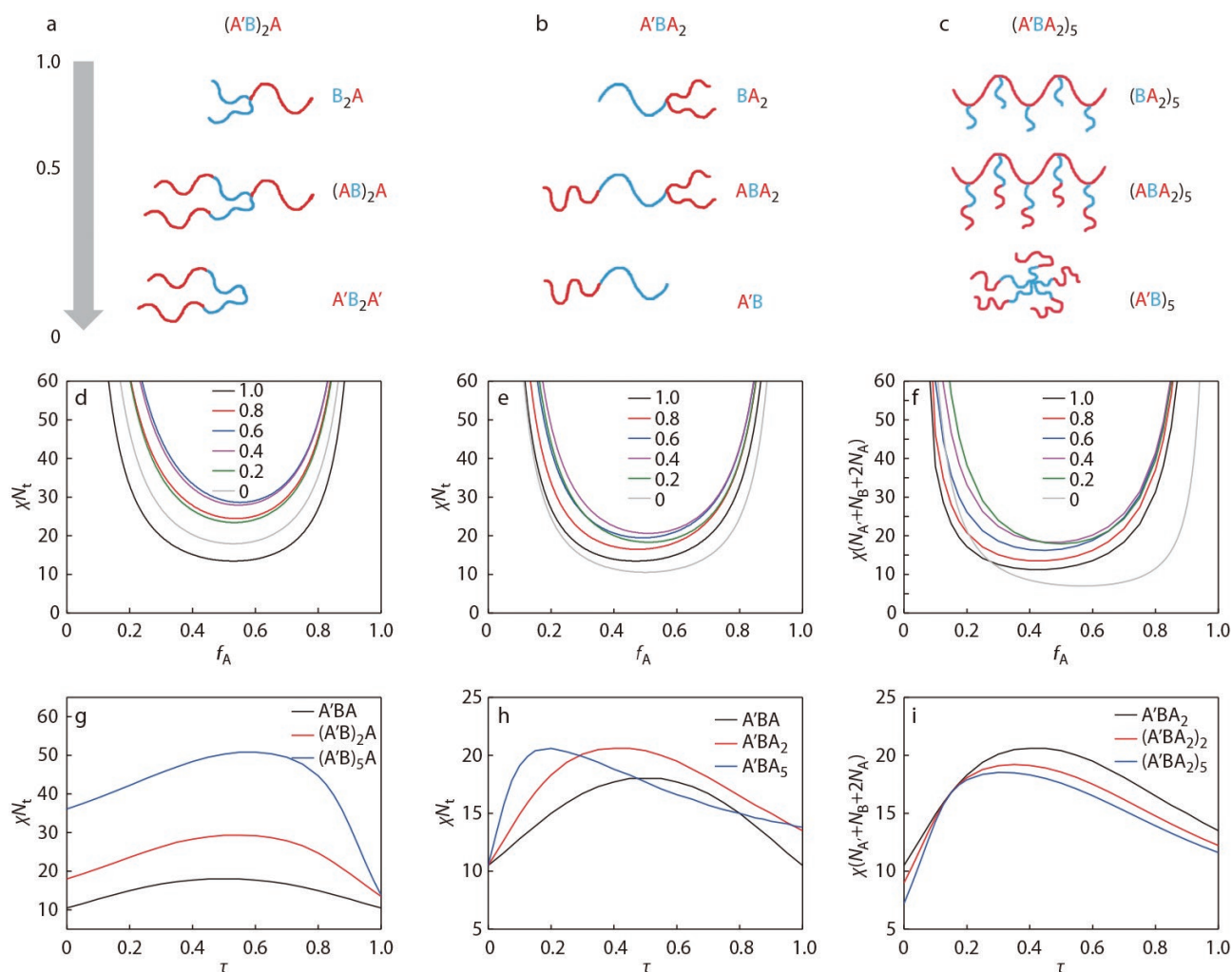


Fig. 5 Effect of the asymmetry ratio of block length on spinodal curves. The miktoarm architectures of $(A'B)_2A$, $A'BA_2$, $(A'BA_2)_5$ with different asymmetry ratios are illustrated in (a), (b), (c), and their spinodal boundaries are shown in (d), (e), (f), respectively. The spinodal curve of each block copolymer is plotted against asymmetry ratio at $f_A=0.5$ in (g), (h), (i), respectively.

mers with $0 < \tau < 1$, the entropy loss of A' and A blocks is $\frac{k}{2} \ln N_{A'} + \frac{k}{2} \ln N_A = k \ln (N_{A'} + N_A) + \frac{k}{2} \ln [\tau(1-\tau)]$, which has a maximum at $\tau=0.5$. The spinodal boundary shifts to higher segregation strengths with τ in $0 < \tau < 0.5$ and drops downward in $0.5 < \tau < 1$ (Fig. 5g). Transforming $A'BA$ to a more complicated structure, i.e. $A'BA_m$, the entropy loss is written as $\frac{k}{2} \ln N_{A'} + \frac{mk}{2} \ln \frac{N_A}{m} = \frac{k}{2} \ln \frac{(N_{A'} + N_A)^{m+1}}{m^m} + \frac{k}{2} \ln [\tau^m(1-\tau)]$, where N_A is the total number of A segment in m blocks. For a selected $A'BA_m$ block copolymer (m is fixed), the second term has a maximum value at $\tau = m/(m+1)$. Thus, for each A block, the maximum entropy loss is at $\tau_{\max} = \frac{1}{1+m}$, which indicates that the $A'BA_m$ has a maximum spinodal boundary when the A' and all A blocks have identical length. This prediction is numerically consistent with the calculation shown in Fig. 5(h). Similar approaches can be applied to even more complicated block copolymers (i.e. $(A'B)_nA$ or $(A'BA_2)_m$), but the details will not be discussed here.

Comparison with Previous Theoretical Methods and Experiments

As a unified model for typical linear and nonlinear block copolymers, this work fully recovers AB , ABA , A_nB_n , $(AB)_n$ and comb-like molecular architectures studied by several different groups independently.^[2,5,8,36] A detailed comparison on AB type block copolymers is given as an example in ESI (Part F). A comparison is also made on comb-like block copolymers, of which the model for the comb-like block copolymers was first developed by Balazs *et al.*^[8] The chains are also assumed to be ideal and satisfy Gaussian statistics in their model (RPA assumption). Despite of different mathematical methods, the calculated spinodal boundaries in this work are fully consistent with the previous results (Part G in ESI).

The model proposed in this work also presents consistency with experimental results. Experiments together with SCFT calculations were carried out in polystyrene-*b*-poly(lactic acid) block copolymers, such as PS-PLA, PS-(PLA)₂, and (PS)₂-(PLA)₂.^[17] Another comparison with experiment is applied in poly(methyl methacrylate)-*b*-poly(*n*-butyl acrylate) (PMMA-

PBA) systems with $(AB)_n$ -type miktoarm block copolymers: $(PMMA-PBA)_1$, $(PMMA-PBA)_4$, $(PMMA-PBA)_{24}$.^[44] Based on the comparison between theory and experiment, one may find that the structure factor is an essential link between theory and experiment: (1) the small angle X-ray (or neutron) scattering curves can be directly fitted with the explicit structure factor of a complicated molecular architecture, and more quantitative parameters (interaction parameter, statistical segment length, etc.) can be extracted from experiment accordingly; (2) since this model is based on the mean-field theory with random phase approximation, the scattering in the mean-field region can be differentiated from the fluctuation-effective region.

One should keep in mind that a spinodal transition curve is very close to, but presents larger segregation strength than that of an ODT boundary in an SCFT phase diagram, except at the critical point ($\chi N_{\text{spinodal}} \geq \chi N_{\text{ODT}}$), which was originally pointed out by Leibler for AB diblock copolymer.^[2] The spinodal point indicates the limit of thermodynamic instability, where a homogeneous system phase separates spontaneously. Only a second-order term is required in the free energy to calculate spinodal transition (Eq. 1). In comparison, at least forth-order terms are included in SCFT to define the ODT, which denotes an equilibrium boundary between ordered spherical phase and disordered state. The gap between the spinodal line and ODT curve manifests the thermodynamic metastable region, which is also correlated with the block copolymer architecture. In the SCFT phase diagram of AB diblock copolymer,^[9] the spinodal line falls in the body-centered cubic (BCC) sphere phase and creates two symmetric metastable regions with respect to $f_A=0.5$ (Part H in ESI). In the SCFT phase diagram of AB_2 miktoarm block copolymer,^[9] the ODT boundary is slightly asymmetric and the order-order transitions (OOT) shifts to large f_A region. So, the metastable region is slightly depressed on the right side in the AB_2 phase diagram (Part I in ESI). For the complex miktoarm block copolymer $(A'B)_3A$,^[30] the SCFT phase diagram is highly asymmetric, where the ordered-phase regions on the left side are enlarged while those on the right side are significantly depressed. The difference between the spinodal and ODT boundary indicates that the metastable region is magnified in the sphere phase on the left side and is vanishingly small in the large f_A region (Part J in ESI). Therefore, the understanding of the spinodal transition complements SCFT studies on the thermodynamics of block copolymers.

Last but not least, the analytical method provided here may also shed light on complicated architectures that are beyond the scope of this work. For example, a dendron-like block copolymer reported recently, where several generations of A blocks are tethered with B blocks, exhibits very interesting phase behavior.^[37] The dendron-like A blocks indicates substantial entropy loss with J2 junctions and the tethered B blocks impart temperate entropy loss with J1 junctions. The spinodal boundary of the dendron-like block copolymers should resemble the $(BA)_n$ stars with large n (Fig. 3c). The simple methodology in this work could be easily extended to other molecular architectures, which may guide researchers to explore more potentially interesting block copolymers.

CONCLUSIONS

To summarize, a block copolymer architecture $[(A'B)_nA_2]_m$ is proposed in this work to elaborate the scattering functions and microphase separation behaviors of typical linear and nonlinear block copolymers. The roles of block number, junction points and asymmetry ratios of block length are the key factors: (1) to affect the entropy loss across the spinodal transition and may result in deflection of spinodal curves; (2) to determine the form factors of each block copolymer at the molecular level ($qR_g \sim 1$). Although only several typical linear and nonlinear block copolymers are demonstrated in this study, the method and conclusions are applicable to other block copolymer architectures. Based on explicit expressions for form factors and structure factors, the model also provides a general guideline for scattering experiments to study block copolymers in solutions or disordered melts.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2544-9>.

ACKNOWLEDGMENTS

This research work is supported by the Fundamental Research Funds for the Central Universities, Nankai University (No. 000082) and the National Natural Science Foundation of China (No. 21973050).

REFERENCES

- Bates, F. S.; Fredrickson, G. H. Block copolymer thermodynamics: theory and experiment. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525–557.
- Leibler, L. Theory of microphase separation in block copolymers. *Macromolecules* **1980**, *13*, 1602–1617.
- Matsen, M. W.; Bates, F. S. Unifying weak- and strong-segregation block copolymer theories. *Macromolecules* **1996**, *29*, 1091–1098.
- Fredrickson, G. H. *The equilibrium theory of inhomogeneous polymers*. Oxford University Press: New York, **2006**.
- Olvera de la Cruz, M.; Sanchez, I. C. Theory of microphase separation in graft and star copolymers. *Macromolecules* **1986**, *19*, 2501–2508.
- Milner, S. T. Chain architecture and asymmetry in copolymer microphases. *Macromolecules* **1994**, *27*, 2333–2335.
- Matsen, M. W.; Schick, M. Microphase separation in starblock copolymer melts. *Macromolecules* **1994**, *27*, 6761–6767.
- Shinozaki, A.; Jasnow, D.; Balazs, A. C. Microphase separation in comb copolymers. *Macromolecules* **1994**, *27*, 2496–2502.
- Matsen, M. W. Effect of architecture on the phase behavior of AB-type block copolymer melts. *Macromolecules* **2012**, *45*, 2161–2165.
- Polymeropoulos, G.; Zapsas, G.; Ntetsikas, K.; Bilalis, P.; Gnanou, Y.; Hadjichristidis, N. 50th Anniversary perspective: polymers with complex architectures. *Macromolecules* **2017**, *50*, 1253–1290.
- Zhulina, E. B.; Borisov, O. V. Effect of block copolymer architecture on morphology of self-assembled aggregates in solution. *ACS Macro Lett.* **2013**, *2*, 292–295.
- Augustine, D.; Hadjichristidis, N.; Gnanou, Y.; Feng, X. Hydrophilic

- stars, amphiphilic star block copolymers, and miktoarm stars with degradable polycarbonate cores. *Macromolecules* **2020**, *53*, 895–904.
- 13 Huang, C. I.; Yu, H. T. Microphase separation and molecular conformation of AB₂ miktoarm star copolymers by dissipative particle dynamics. *Polymer* **2007**, *48*, 4537–4546.
 - 14 Teng, X.; Zhang, P.; Liu, T.; Xin, J.; Zhang, J. Biobased miktoarm star copolymer from soybean oil, isosorbide, and caprolactone. *J. Appl. Polym. Sci.* **2020**, *137*, 48281.
 - 15 Zhou, F.; Zhou, Q.; Tian, H.; Li, C.; Zhang, Y.; Fan, X.; Shen, Z. Synthesis and self-assembly of a triarm star-shaped rod-rod block copolymer. *Chinese J. Polym. Sci.* **2015**, *33*, 709–720.
 - 16 Bates, M. W.; Barbon, S. M.; Levi, A. E.; Lewis III, R. M.; Beech, H. K.; Vonk, K. M.; Zhang, C.; Fredrickson, G. H.; Hawker, C. J.; Bates, C. M. Synthesis and self-assembly of AB_n miktoarm star polymers. *ACS Macro Lett.* **2020**, *9*, 396–403.
 - 17 Shi, W.; Tateishi, Y. C.; Li, W.; Hawker, C. J.; Fredrickson, G. H.; Kramer, E. J. Producing small domain features using miktoarm block copolymers with large interaction parameters. *ACS Macro Lett.* **2015**, *4*, 1287–1292.
 - 18 Ji, S. X.; Wan, L.; Liu, C. C.; Nealey, P. F. Directed self-assembly of block copolymers on chemical patterns: a platform for nanofabrication. *Prog. Polym. Sci.* **2016**, *76*–127.
 - 19 Pang, Y. Y.; Jin, X. S.; Huang, G. C.; Wan, L.; Ji, S. X. Directed Self-assembly of styrene-methyl acrylate block copolymers with sub-7 nm features via thermal annealing. *Macromolecules* **2019**, *52*, 2987–2994.
 - 20 Jiang, Y.; Hadjichristidis, N. pH-Responsive AIE-active polyethylene-based block copolymers. *Chinese J. Polym. Sci.* **2019**, *37*, 930–935.
 - 21 Bai, Y.; Xie, F.; Tian, W. Controlled self-assembly of thermo-responsive amphiphilic H-shaped polymer for adjustable drug release. *Chinese J. Polym. Sci.* **2018**, *36*, 406–416.
 - 22 Liu, Z.; Zhang, G. Preparation of Janus hybrid gold nanoparticles based on asymmetric star polymers. *J. Funct. Polym.* **2020**, *33*, 342–349.
 - 23 Shin, J. J.; Kim, E. J.; Ku, K. H.; Lee, Y. J.; Hawker, C. J.; Kim, B. J. 100th Anniversary of macromolecular science viewpoint: block copolymer particles: tuning shape, interfaces, and morphology. *ACS Macro Lett.* **2020**, *9*, 306–317.
 - 24 Zhu, Y.; Burgaz, E.; Gido, S. P.; Staudinger, U.; Weidisch, R.; Uhrig, D.; Mays, J. W. Morphology and tensile properties of multigraft copolymers with regularly spaced tri-, tetra-, and hexafunctional junction points. *Macromolecules* **2006**, *39*, 4428–4436.
 - 25 Burns, A. B.; Register, R. A. Mechanical properties of star block polymer thermoplastic elastomers with glassy and crystalline end blocks. *Macromolecules* **2016**, *49*, 9521–9530.
 - 26 Lynd, N. A.; Oyerokun, F. T.; O'Donoghue, D. L.; Handlin, D. L. Jr.; Fredrickson, G. H. Design of soft and strong thermoplastic elastomers based on nonlinear block copolymer architectures using self-consistent-field theory. *Macromolecules* **2010**, *43*, 3479–3486.
 - 27 Shi, W.; Lynd, N. A.; Montarnal, D.; Luo, Y.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Hexemer, A. Toward strong thermoplastic elastomers with asymmetric miktoarm block copolymer architectures. *Macromolecules* **2014**, *47*, 2037–2043.
 - 28 Shi, W.; Hamilton, A. L.; Delaney, K. T.; Fredrickson, G. H.; Kramer, E. J.; Ntaras, C.; Avgeropoulos, A.; Lynd, N. A.; Demassieux, Q.; Creton, C. Aperiodic “bricks and mortar” mesophase: a new equilibrium state of soft matter and application as a stiff thermoplastic elastomer. *Macromolecules* **2015**, *48*, 5378–5384.
 - 29 Liu, Y. X.; Delaney, K. T.; Fredrickson, G. H. Field-theoretic simulations of fluctuation-stabilized aperiodic “bricks-and-mortar” mesophase in miktoarm star block copolymer/homopolymer blends. *Macromolecules* **2017**, *50*, 6263–6272.
 - 30 Lequeieu, J.; Koeper, T.; Delaney, K. T.; Fredrickson, G. H. Extreme deflection of phase boundaries and chain bridging in A(BA)_n miktoarm star polymers. *Macromolecules* **2020**, *53*, 513–522.
 - 31 Levi, A. E.; Fu, L.; Lequeieu, J.; Horne, J. D.; Blankenship, J.; Mukherjee, S.; Zhang, T.; Fredrickson, G. H.; Gutekunst, W. R.; Bates, C. M. Efficient synthesis of asymmetric miktoarm star polymers. *Macromolecules* **2020**, *53*, 702–710.
 - 32 Xie, Q.; Qiang, Y.; Chen, L.; Xia, Y.; Li, W. Synergistic effect of stretched bridging block and released packing frustration leads to exotic nanostructures. *ACS Macro Lett.* **2020**, *9*, 980–984.
 - 33 Chen, L.; Qiang, Y.; Li, W. Tuning arm architecture leads to unusual phase behaviors in a (BAB)₅ star copolymer melt. *Macromolecules* **2018**, *51*, 9890–9900.
 - 34 Xie, N.; Li, W. H.; Qiu, F.; Shi, A. C. σ Phase formed in conformationally asymmetric AB-type block copolymers. *ACS Macro Lett.* **2014**, *3*, 906–910.
 - 35 Jiang, W.; Qiang, Y.; Li, W.; Qiu, F.; Shi, A. C. Effects of chain topology on the self-assembly of AB-type block copolymers. *Macromolecules* **2018**, *51*, 1529–1538.
 - 36 Ji, X.; Li, W. Effect of chain architectures on the domain spacing of block copolymers with equivalent segregation degrees. *Phys. Chem. Chem. Phys.* **2020**, *22*, 17824–17832.
 - 37 Qiang, Y.; Li, W.; Shi, A. C. Stabilizing phases of block copolymers with gigantic spheres via designed chain architectures. *ACS Macro Lett.* **2020**, *9*, 668–673.
 - 38 Hamley, I. W.; Castelletto, V. Small-angle scattering of block copolymers: in the melt, solution and crystal states. *Prog. Polym. Sci.* **2004**, *29*, 909–948.
 - 39 Mori, K.; Tanaka, H.; Hashimoto, T. Scattering functions for disordered two-component polymer systems including block polymers. *Macromolecules* **1987**, *20*, 381–393.
 - 40 Yilmaz, G.; Yagci, Y. Mechanistic transformations involving radical and cationic polymerizations. *Chinese J. Polym. Sci.* **2020**, *38*, 205–212.
 - 41 Lynd, N. A.; Meuler, A. J.; Hillmyer, M. A. Polydispersity and block copolymer self-assembly. *Prog. Polym. Sci.* **2008**, *33*, 875–893.
 - 42 Matsen, M. W.; Thompson, R. B. Equilibrium behavior of symmetric ABA triblock copolymer melts. *J. Chem. Phys.* **1999**, *111*, 7139–7146.
 - 43 Matsen, M. W. Equilibrium behavior of asymmetric ABA triblock copolymer melts. *J. Chem. Phys.* **2000**, *113*, 5539–5544.
 - 44 Wang, Y.; Zhong, M.; Park, J. V.; Zhukhovitskiy, A. V.; Shi, W.; Johnson, J. A. Block co-polyMOCs by stepwise self-assembly. *J. Am. Chem. Soc.* **2016**, *138*, 10708–10715.