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

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Electronic Supplementary Information

Abstract This work uses a block copolymer architecture \([(A'B)_nA]_{nm}\) 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 ABA triblock, miktoarm stars of AB, A, B, (AB)\(_n\), (A'B)\(_n\), A'B\(_n\), and multi-graft combs of (B\(_n\)A)\(_m\) and \([(A'B)_nA]_{nm}\). 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

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 \((\chi)\), and the volume fraction \((\phi)\). 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.\(^18\)–\(^26\)

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 copolymer.\(^26\)–\(^36\) The A\(_n\)B\(_n\) 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)\(_n\) 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
molecular architecture. The scattering function for diblock copolymers was first developed by Leibler in the context of mean field theory with random phase approximation. 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, ABA, and (AB)n, miktoarm stars. An explicit formula of scattering function is certainly an essential link between theories and experiments in disordered melts and in polymer solutions. 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)n]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)n, 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, ABA, AAB, ABA, and AB stars of diblock arms (AB)n; stars of mixed homo/diblock arms (A'B)n, and comb-like block copolymers (BnA)n and (A'B)n. 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,

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

(1)

where the \(< >\) 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,

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

(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 where $\frac{\partial^2 G}{\partial \phi^2} = 0$.

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

$$\langle \delta \phi_j \delta \phi_k \rangle = S(\mathbf{r}_j)$$

(3)

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

$$S(q) = \int \mathbf{r}_j \exp (i \mathbf{q} \cdot \mathbf{r}_j) S(\mathbf{r}_j)$$

(4)

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

$$I(q) = (l_s - l_0)^2 S(q)$$

(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, $l_s$ and $l_0$ are scattering length densities of each component. The $q$ is related to the scattered angle $\theta$ and the wavelength of the beam $\lambda$ in scattering experiment by the relation $q = \frac{4 \pi \theta}{\lambda \sin \frac{\theta}{2}}$.

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 $r_j$ and the $k$th segment at point $r_k$,

$$S(q) = \frac{1}{N} \sum_{j=0}^{N} \sum_{k=0}^{N} \langle \exp (i \mathbf{q} \cdot \mathbf{r}_j) \rangle djdk$$

(6)

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

$$S(q) = \frac{1}{N} \sum_{j=0}^{N} \left[ \frac{q^2 b^2}{6} N + \exp \left( -\frac{q^2 b^2}{6} N \right) - 1 \right] = \frac{1}{N} g(N)$$

(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)n]m and its derivatives, including a miktoarm model (A'B)n, AB diblocks, ABA linear triblocks, miktoarm stars of homoblocks AB, A or ABA, miktoarm stars of diblocks (A'B)n, miktoarm stars of homo/diblock arms (A'B)n, A or ABA, multi-graft combs (BA)n, and (A'B)n. Specific block copolymer architectures with $n=m=w=3$ are drawn for illustration.](https://doi.org/10.1007/s10118-021-2544-9)
The scattering function of a two-component block copolymer was first developed by Leibler,[2]

\[ S(q) = \frac{W}{S' - 2qW} \]

(9)

\[ S' = S_{AA}^* + S_{BB} + 2S_{AB}^* \]

(10)

\[ W = S_{AA}^* S_{BB}^* - (S_{AB}^*)^2 \]

(11)

The interaction between the two chemical species is denoted by \( \chi \). 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, e.g. diblock copolymers, or binary polymer blends.[39]

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

\[ N = m(n N_1 + n N_2 + 2 N_3) \]  

(12)

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

\[ f_A = \frac{n N_1 + 2 N_3}{n N_1 + n N_2 + 2 N_3} \]  

(13)

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

\[ \tau = \frac{N_j}{N_1 + N_3} \]  

(14)

The pair correlations of AA, BB and AB are:

\[ S_{AA}^* = S_{AA} + n S_{AA}' + n(n - 1) \sum_{ij=1} S_{A_A'} + n^2 \sum_{i=1} S_{AA}^2 (A_A') \]  

(15)

\[ S_{BB}^* = n n S_{BB} + n(n - 1) \sum_{ij=1} S_{B_B'} + n^2 \sum_{i=1} S_{BB}^2 (B_B') \]  

(16)

\[ S_{AB}^* = n m S_{AB} + n(n - 1) \sum_{ij=1} S_{A_B'} + n^2 \sum_{i=1} S_{AB}^2 (A_B') \]  

(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

\[ S_{AA} = N_1^{-1} g(2n N_1) \]

(18)

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

\[ S_{A_A'} = N_1^{-1} g(N_1) \]

(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

\[ S_{A_A'}^* = \frac{1}{2}(S_{A_A'}^0 + S_{A_A'}^0 - S_{A_A'}^0 - S_{A_A'}^0 + S_{A_A'}^0 + S_{A_A'}^0) \]

(20)

where

\[ S_{A_A'}^0 = N_1^{-1} g(2n N_1 + 2 N_2 + 2|j - i| N_3) \]

(21)

\[ S_{A_A'}^* = N_1^{-1} g(N_1 + 2 N_2 + 2|j - i| N_3) \]

(22)

\[ S_{A_A'}^* = N_1^{-1} g(2n N_1 + 2 N_2) \]

(23)

The correlation function of A and A’ segments at the \( n \)th junction point is

\[ S_{AA'}^* = \frac{1}{2}(S_{A_A'}^0 + S_{A_A'}^0 - S_{A_A'}^0 - S_{A_A'}^0 + S_{A_A'}^0 + S_{A_A'}^0) \]

(24)

where

\[ S_{A_A'}^0 = N_1^{-1} g(N_1 + N_2 + 2 N_3) \]

(25)

\[ S_{A_A'}^* = N_1^{-1} g(2n N_1 + N_2 + 2 N_3) \]

(26)

\[ S_{A_A'}^* = N_1^{-1} g(N_1 + N_2) \]

(27)

\[ S_{A_A'}^* = N_1^{-1} g(2 N_1 + 2|j - i| N_3) \]

(28)

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

\[ S_{BB}^* = N_1^{-1} g(N_2) \]

(29)

The correlation of a B segment in the \( i \)th junction point and a B segment in the \( j \)th junction point is

\[ S_{BB}^* = \frac{1}{2}(S_{B_B'}^0 + S_{B_B'}^0 - S_{B_B'}^0 - S_{B_B'}^0 + S_{B_B'}^0 + S_{B_B'}^0) \]

(30)

where

\[ S_{B_B'}^0 = N_1^{-1} g(N_1 + N_2 + 2 N_3) \]

(31)

\[ S_{B_B'}^* = N_1^{-1} g(2 N_1 + 2|j - i| N_3) \]

(32)

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

\[ S_{A_B'}^* = \frac{1}{2}(S_{A_B'}^0 + S_{A_B'}^0 - S_{A_B'}^0 - S_{A_B'}^0 + S_{A_B'}^0 + S_{A_B'}^0) \]

(33)

The correlation function of an A’ segment in the \( n \)th junction point and a B segment in the \( j \)th junction point is

\[ S_{A_B'}^* = \frac{1}{2}(S_{A_B'}^0 + S_{A_B'}^0 - S_{A_B'}^0 - S_{A_B'}^0 + S_{A_B'}^0 + S_{A_B'}^0) \]

(34)

The correlation function of an A segment and a B segment at the \( n \)th junction point is

\[ S_{AB}^* = \frac{1}{2}(S_{A_B'}^0 + S_{A_B'}^0 - S_{A_B'}^0 - S_{A_B'}^0 + S_{A_B'}^0 + S_{A_B'}^0) \]

(35)

where

\[ S_{A_B'}^0 = N_1^{-1} g(2 N_1 + 2 N_2 + 2 N_3) \]

(36)

\[ S_{A_B'}^* = N_1^{-1} g(2 N_1 + 2 N_2 + 2 N_3) \]

(37)

\[ S_{A_B'}^* = N_1^{-1} g(2 N_1 + 2 N_2 + 2 N_3) \]

(38)

\[ S_{A_B'}^* = N_1^{-1} g(2 N_1 + 2 N_2 + 2 N_3) \]

(39)

The repeat unit \( (A'B)_n A_2 \) in this comb-like block copolymer \( (A'B)_m A_2 \) can be slightly modified to get a miktoarm star of \( (A'B)_m A_2 \) (Fig. 1), which consist of \( n \) arms of A’B diblock and \( w \) arms of A block. The scattering function of \( (A'B)_m A_2 \) 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 $(A’B)_m$ miktoarm star of homoblocks $A_mB_n$, or $A_nB_m$ multi-graft combs $(BA)_m$, and $(A’BA)_m$. 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 $[(A’B)_{2m}]$ to the $(BA)_{2m}$ 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 $\theta$ 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

$$F(q) = \frac{S^2(q)}{S^2(0)} = \frac{1}{N_q} S^2(q)$$ \(\text{(40)}\)

The form factors of $A_mB_n$ block copolymers are shown in Fig. 2(a). The form factors of all $A_mB_n$ block copolymers converge to 1 at $qR_g<1$. At $qR_g>1$, the AB diblock copolymer exhibits a characteristic power index $F(q)\sim q^{-\alpha}$, which represents the topology of a linear Gaussian chain. Increasing the number of arms in $A_mB_n$, 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 $qR_g^{-1}$, while still behaves as a Gaussian chain $F(q)\sim q^{-2}$ at $qR_g^{-2}$, 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 $(B_mB_n)_m$ (Part C in ESI).

**Fig. 2** Form factors of block copolymers. The form factors of $A_mB_n$ block copolymers are shown in (a). The form factors of an $A_mB_n$ and an $(AB)_m$ block copolymer are shown by a $F(q)\sim qR_g$ plot in (b) and a $F(q)\sim q$ plot in the inset. The form factors of $(BA)_m$ block copolymers are shown by a $F(q)\sim qR_g$ plot in (c) and a $F(q)\sim qR_g$ plot in the inset. The block lengths of $N_1=N_2=500$ and $b=0.5$ nm are used in (a–c). The radius of gyration of one A strand, $R_g=[(N_1+N_3)/6]^{1/2}b$, is used in (b) to rescale the form factors. The radius of gyration of one A strand, $R_g=[(N_1+N_3)/6]^{1/2}b$, 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 $A’B$ 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 $t=0$ (diblock) is used to rescale the form factors.

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The (AB)_n block copolymers generally have different form factors from A_B_n and (AB)_2n are very similar and scalable. An A_B_2n and (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_B_2n (Part D in ESI). But the form factors of (AB)_10 and A_B_2n fall on a normalized curve (Fig. 2b), if the radius of gyration of one AB diblock (R_g = ((N_A+N_B)/6)^1/2) 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)_n each unit is a Y-shape BA 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)-q^2 is well maintained. Accordingly, the form factors could be further rescaled by the repeat number q^m 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, (BA)_3 and (BA)_10 almost fall on a normalized curve in the whole q range except very slight discrepancy at q^m R_g<1. In comparison, the form factor of BA2 exhibits significant discrepancy at q^m R_g>1. The discrepancy indicates that the effect of chemical connectivity of BA2 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 miktoarm with different asymmetry ratios (r, Eq. 14) is shown in Fig. 2(d). Variation of r affects the form factor slightly at qR_g<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<1 and the topological feature remains Gaussian at qR_g>1. The effect of molecular architecture is significant at qR_g<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 wavenumber 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_B_n and (BA)_n star block copolymers are well studied architectures in literature and are reproduced here for comparison.[3,4] The A_B_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 \(q=0.5\) and \(\chi(N_A+N_B)=10.5\). The (BA)_n molecules share one juncti (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 (BA)_2_j miktoarms 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_B_A (BA)_n and (BA)_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 (BA)_2_A stays very close to A_B_A at low \(f_A\) region and locates between A_B_A and (BA)_n at high \(f_A\) region, which indicates that the connection of two A blocks in (BA)_2_A by one J2 junction plays trivial effect at small \(f_A\) compared with the J2 junction in (BA)_2 while J1 junction in (BA)_2_A takes effect at high \(f_A\), but is less significant than the role of J1 in A_B_A.

The BA2 (or AB_A) miktoarm is a typical example that the number of A and B blocks is unequal at J1. The spinodal boundary of BA2 is slightly asymmetric (Figs. 4a and 4b). Combination of more BA2 at J1 (BA)_2 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 BA2 in series by the end of A block (J2), that is the comb-like block architecture (BA)_2 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.[43] The linear A BA miktoarm stars of (A'B)_n A and A'BA_n, and comb-like (A'BA)_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 \(r=1\) or \(r=0\); it returns to a symmetric triblock copolymer ABA at \(r=0.5\). Thus, the spinodal boundaries shift upward from a symmetric curve of AB at a lower \(\chi(N)\), to asymmetric curves of ABA at higher \(\chi(N)\) at \(0<\tau<0.5\).[43] The spinodal lines at \(r=0.5\pm 0.05(0.55 \pm 0.005)\) completely overlap.

For the miktoarm star (A'B)_n A and (A'B)_{2n}, the structure recedes to an AB type block copolymer at \(r=1\); it returns to a linear triblock copolymer A'BA' (equivalent to ABA) at \(r=0\). Increasing the length of two A' blocks in an (A'B)_2 A block.
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 AB.

For the miktoarm star A’BA \(_2\) (Figs. 5b and 5e), the structure reduces to an BA \(_2\) 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’BA \(_2\) 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 AB.

The (A’BA \(_2\)) \(_5\) 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 (BA \(_2\)) \(_5\) at \(\tau = 1\), where A is the backbone with 5 grafted B blocks; it returns to a miktoarm star block copolymer (A’B) \(_2\) 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) \(_n\) leads to significant increase of the spinodal boundary and deflection of the upper point to larger \(\tau\). The spinodal points of the AB, 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 \(_n\) (Fig. 5h), in contrast, does not increase the spinodal

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**Fig. 3** Molecular architectures of A\(_4\)B(A), (BA)\(_4\) and (B\(_2\)A\(_2\))\(_2\) (a); Spinodal boundaries of A\(_n\)B\(_n\) (b), (BA)\(_n\) (c) and (B\(_2\)A\(_2\))\(_n\) (d); Comparison of spinodal boundaries of AB, A\(_n\)B\(_n\) (BA)\(_4\) and (B\(_2\)A\(_2\))\(_2\) (e).
boundary much, but significantly deflects the maximum to lower r. All molecular structures recover to A'B at r=0, and its spinodal point is slightly lower than that of BAm at r=1. Increase in the repeat number of the comb-like structure (A'BAm) (Fig. 5i), however, decreases spinodal boundaries slightly and deflects the maximum to lower r. It is interesting to find that all curves share a point at r=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)m at r=0 is lower than that of an BA2 unit in (BA2)m at r=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,

$$\Delta S = \Delta S_A + \Delta S_B + \Delta S_J$$

(41)

where $\Delta S_A$, $\Delta S_B$, $\Delta S_J$ 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 $kln(V)$. Suppose each junction point occupies a volume of $v$ in the total volume $V$, the translational entropy loss of a junction point is $kln(V/v)$, where $v=V$ at the critical point and $v<V$ otherwise.

For the ABm type miktoarm block copolymer, increasing number of arms (n) increases the entropy loss of the B blocks by $nk^2\ln(\chi_{BA}N_B)$, while the entropy loss of the A block and the junction point does not change. Thus, larger segregation strengths (large $\chi_{BA}$ values) are required to counteract the entropy effect and initiate spinodal transition. Similarly, for the A,Bn 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 $nk^2\ln(\chi_{NA}N_B)$. The normalized entropy loss for each AB diblock in A,Bn is then $k^2\ln(\chi_{BA}N_B) + k^2\ln(\chi_{NA}N_B)$. For the A,Bn 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). Special concern should be taken at $n_0=0.5$, where the block copolymer crosses the critical point with $V=V_f$. Accordingly, the normalized spinodal boundary of $\chi(NA+NB)$ is symmetric, independent of n at $n_0=0.5$ 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 $nk^2\ln(\chi_{BA}N_B)$ and that of the J1 is $nk^2\ln(V_f)$.

The entropy loss of the B blocks is symmetric, independent of n at $n_0=0.5$ and decreases with n otherwise (Fig. 3c).

The (BA2)m comb-like block copolymers contain m junctions of J1 and (m−1) junctions of J2 (m≥2). The repeated growth of BA2 only affects the entropy of J2. The first J2 can be freely placed in the volume of $V_{F_{BA}}$, while the other J2 points are subsequently correlated in a nearby volume of $V_{BA}$ that is accessible by one A block. $V_{F_{BA}}$ scales to $\sim R_{eq}^3$ and is much smaller than $V_{F_{BA}}$. The normalized entropy loss of each BA2 unit is therefore $k^2\ln(V_{F_{BA}}) + (m-2)k^2\ln(V_{F_{BA}})$, which is dominated by the first term, decreases with m and increases with $f_A$. Thus, the spinodal curves of $\chi(2NA+NB)$ 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-
mers with $0<\tau<1$, the entropy loss of $A'$ and $A$ blocks is
\[ k \frac{1}{2} \ln N_A' + k \frac{1}{2} \ln N_A = k \ln (N_A' + N_A) + k \frac{1}{2} \ln (1 - \tau), \]
which has a maximum at $\tau=0.5$. The spinodal boundary shifts to higher segregation strengths with $\tau$ 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
\[ \frac{k}{2} \ln N_A + \frac{m}{2} \ln \frac{N_A}{m} = \frac{k}{2} \ln \left( \frac{N_A'}{N_A} \right)^{m+1} + \frac{k}{2} \ln \left( \frac{m}{1 - \tau} \right), \]
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 $\tau_{\text{max}} = \frac{1}{1 + m}$, 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. $(A'B)_m$ or $(A'BA)_m$), 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 $AB$, $ABA$, $A_mB_m$ and comb-like molecular architectures studied by several different groups independently.

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. 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($\alpha$-lactic acid) block copolymers, such as PS-PLA, PS-(PLA)$_2$, and (PS)$_2$-(PLA)$_2$. Another comparison with experiment is applied in poly(methyl methacrylate)-$b$-poly(n-butyl acrylate) (PMMA-...
CONCLUSIONS

To summarize, a block copolymer architecture \([A'B_{\eta}A]\) 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 \((q_{ODT})^{-1}\). Although only several typical linear and nonlinear block copolymers are demonstrated in this study, the methodology 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

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