# Ring gradient copolymers as amphiphiles in their ternary blends with two linear homopolymers

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ABSTRACT

Phase equilibria in a ternary blend of linear A/B homopolymers of equal sizes and a symmetric A-co-B ring gradient copolymer as an amphiphile with $\alpha$ as the ratio of their chain sizes are investigated in the mean-field picture. The monomer sequence on the copolymer chain is taken in between a step gradient and a fully linear gradient, to which a gradient number $\lambda = 0$ and 1 are assigned, respectively. Along the isopleths of equal homopolymer amounts, the resultant phase diagrams for the blends are to be built from multicritical points such as Lifshitz or bulk tricritical point depending on $\alpha$ and $\lambda$. It is shown that the copolymer of doubling-back ring topology or augmented gradient sequence in the ternary blend narrows the feasible region for the Lifshitz point. The ternary blend accordingly becomes more prone to macrophase separation starting from the tricritical point and the stabilization of its lamellar mesophase is more shrunken than that containing the copolymer of linear topology or diminished gradient sequence.

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## 1. Introduction

Blending currently existing polymers to form polymer alloys is a relatively convenient and economical route to creating new useful materials. The properties of thus-formed polymer blends can be tuned by changing the compositions of their constituent materials [1–5]. A majority of polymer pairs are immiscible. To avoid macrophase separation between blended homopolymers, amphiphilic copolymers are often added in order to stabilize the blends and to improve their mechanical properties by reduction in interfacial tensions [6–9].

Such copolymers from two different monomers can have limitless numbers of their sequences. This feature is a definite merit in a material design perspective, considering that copolymer melts and blends containing copolymers are affected in their phase behaviors by monomer sequences along copolymer chain contours [10–24]. Among vast choices, recent efforts have been exerted to understand the properties of linear gradient copolymers, in particular, in the molten state [12,14,19], in solutions [21,25], and as interfacial layers [24] and brushes [22,23]. Wang et al. studied the phase behavior of the blends of two linear homopolymers and the linear gradient copolymers [13], where the changes in the phase diagrams of the blends upon a fixed chain size ratio between the constituent polymers were considered with varying the composition gradient length.

Meanwhile, previous investigations have shown that the topological shapes of polymers bring nontrivial impact to their various physical properties [26–29]. Nonetheless, less attention has been paid to blends containing ring copolymers and/or ring homopolymers, in contrast to blends of linear homopolymers and copolymers. Some binary blends with one ring component exhibited significantly enhanced miscibility and their two-phase region was shrunken, when compared to the corresponding linear homopolymer blends [30–32]. Relevant to this issue, ring copolymers in a solution have been explored experimentally and also theoretically [33–35]. The θ-temperature for the ring copolymer was also found to be lower than that for the linear counterpart [33]. Benmouna et al. reported the scattering properties and phase behavior of the ternary blends with two ring homopolymers and a ring copolymer [36]. They found that the blends show the enhanced compatibility. In their work, only phase stability was calculated and the full phase diagram for the ternary blends was not made [36]. Recently, the change in the interfacial properties of the blends of two linear homopolymers with the addition of a ring gradient copolymer was reported by the present authors [37].

In this work, we discuss the role of monomer sequences and ring topology of a copolymer in controlling blend properties. The systems of our interest are the ternary blends of A/B linear

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homopolymers and an A-co-B *ring gradient copolymer* as an amphiphile. Various gradient sequences for the copolymer chain contour are treated in between a unit-step gradient (diblock) and a fully linear gradient, to which a number $\lambda = 0$ and 1 are respectively assigned for the description of the gradient length. The phase equilibria of the blends are scrutinized through random-phase approximation (RPA) [10,38—40] and self-consistent field theories (SCFT) [41—46]. We provide a procedure to analytically obtain conditions for Lifshitz points for the ternary blends, which appear when lamellae-to-disorder critical points starting from the molten copolymers coincide with bulk critical points stemming from the A/B homopolymer blend. Lifshitz tricritical points, at which three different macroscopic critical points from A/B, A/A-co-B, B/A-co-B blends meet together with the Lifshitz points, are also to be determined. A series of phase diagrams for the blends at different chain size ratios between homopolymers and copolymers with two extremes, $\lambda = 0$ and 1, are calculated along the isopleths with the equal amounts of A and B homopolymers. Still, it is shown that valuable conclusions can be drawn in connection with the conditions for those multicritical points.

## 2. Theoretical methods

### 2.1. Model

Consider an incompressible ternary blend consisting of $n_{HA}$ linear A and $n_{HB}$ linear B homopolymer chains, and also $n_C$ A-co-B ring copolymer chains in a system volume $V$. Their chain lengths are respectively denoted as $N_{HA}$, $N_{HB}$, and $N_C$. It is assumed that all the segments in the system have the identical diameter $\sigma$. The A and B homopolymers in the blend are assumed to have the same chain length $N_{HA} = N_{HB} = N_H$. The copolymer is of the symmetric composition, which means that the volume fraction $f_A$ of A monomers on the copolymer chain is fixed to 0.5. The ratio of chain lengths between the homopolymers and the copolymer is denoted as $\alpha = N_H/N_C$. In the bulk state, each constituent possesses the volume fraction $\phi_j = n_j N_j / \sum n_i N_i$, where $j = $ HA, HB, and C. In this work, we probe our ternary blend system along the isopleths with $\phi_{HA} = \varphi_{HB}$. A and B monomers are incompatible, which is signified by the so-called effective Flory—Huggins interaction parameter $\chi$.

The topologies of ring gradient copolymers in our study are the same as in Fig. 1 of our previous paper [37]. The extent of the composition gradient length along the copolymer chain contour is described by a number $\lambda$, which is defined as the ratio of the length of the composition gradient part to the contour length. So, the copolymers with $\lambda = 0$ and 1 correspond to diblock rings with a unit step gradient and to fully gradient rings, respectively. The local volume fraction of A or B monomers is assumed to vary linearly in the gradient region for the copolymer of $\lambda > 0$. In the calculational procedure, the gradient region is constructed in a multiblock way [18], where it is divided into 200 identical subparts. Each subpart is treated as a small diblock copolymer with its own $\bar{f}_A$ that varies along from 0 to 1.

Under the fixed isoplethic constraint, the ternary blend exhibits several multicritical points such as Lifshitz, tricritical, and Lifshitz tricritical points. The Lifshitz point appears when the lamellae-to-disorder critical point starting from the molten copolymer coincides with the bulk critical point stemming from the A/B homopolymer blend. The tricritical point is defined by the situation when macroscopic critical points from three different pairs such as A/B, A/A-co-B, B/A-co-B blends meet together. The Lifshitz tricritical point is then revealed if the Lifshitz and tricritical points merge into one.
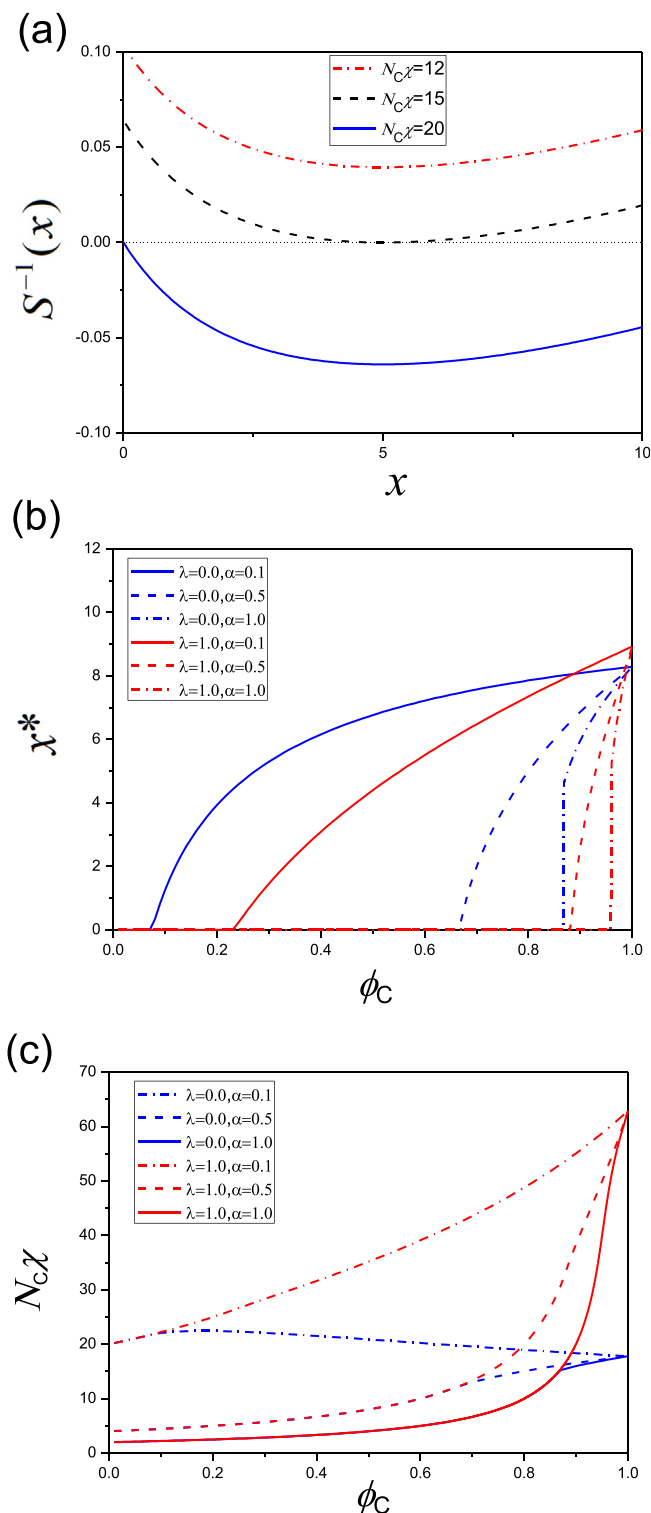


**Fig. 1.** (a) Inverse structure factor $S^{-1}(x)$ for an incompressible A/B/A-co-B ($\lambda = 0$ and $\alpha = 0.5$) ternary blend at indicated $N_C\chi$'s plotted against squared wave number $x$ ($= k^2 R_G^2$), where $R_G$ is the radius of gyration of a reference linear chain with $N_C$ monomers. The copolymer volume fraction $\varphi_C$ is fixed to 0.8, and homopolymer volume fraction is symmetric as $\varphi_A = \varphi_B$. (b) Characteristic squared wave number $x^*$ as a function of $\phi_C$ for the six blends in Table 1. (c) $N_C\chi$ for Scott's line (A/B critical points) and that for lamellar mesophase critical line plotted against $\phi_C$ for the six ternary blends in Table 1.