



# Phase diagrams of ABC linear triblock copolymers under nanopore confinements

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## ABSTRACT

The phase diagrams of triblock copolymers in cylindrical nanopores are investigated using the real-space self-consistent field theory in a two-dimensional space. We concentrate on pores with neutral surfaces and invariable diameters, whose rich variety of phases are considered to originate from pure geometric frustration. A series of triangular phase diagrams are constructed by varying the volume fractions for several sets of interaction parameters. These diagrams are sorted into three categories according to their interaction parameters. The confined phase diagrams exhibit several characteristic features that differ from those observed in the bulk. First, a rich variety of geometric frustration phases with strong symmetries, such as cylindrical and square, are observed in the triangular phase space because of the symmetry constraint in the geometric boundary. Second, the frustrated phases present some novel and complex features compared with those in the bulk, demonstrating that the confined morphologies much more sensitively depend on the subtle variation in the binary interaction parameters than those in the bulk. Meanwhile, the entropic energies of the symmetric melts with equal end block volume fractions are investigated to further understand the geometric frustration phase behaviors in the triangular phase diagrams. The reasonable formation mechanisms of the frustration phases are also discussed.

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## 1. Introduction

The self-assembled nanostructures of block copolymers have attracted considerable attention because of their potential applications in a wide range of fields, from materials science to biology [1,2], especially in nanotechnology [3–5]. The nanostructures of block copolymers are generally controlled by their polymer and confinement parameters, which are then used to construct phase diagrams. These phase diagrams can provide a convenient method of identifying the novel nanostructures and be used to investigate morphological transition process of block copolymers. Consequently, constructing phase diagrams is a vital approach to exploring morphological transition mechanisms. These transition mechanisms will instruct us to produce our desired novel functional nano materials.

In bulk, the phase diagrams of diblock copolymers are mainly determined using two tunable molecular parameters, namely,  $f_A$ , which is the volume fraction of block A, and  $\chi_{AB}N$ , which is the interaction parameter between the distinct A and B species. The  $\chi N - f$  phase diagrams for the bulk diblock copolymers have

been extensively investigated using theories, simulations, and experiments [6–14]. The phase transitions from lamellae (L) to cylinders (C) to spheres (S) occur because of the spontaneous curvature produced as the asymmetry in the diblock composition increases [11,14]. Several complex phases, gyroid (G), perforated lamellar (PL), and double diamond (D), have curvatures between those of L and C, and therefore they compete for stability along the L/C boundary. Nevertheless, only G is predicted as a stable phase, which occurs over only a narrow range of  $f$  in the  $\chi N - f$  phase diagram [11]. These morphologies are confirmed through transmission electron microscopy (TEM) using polystyrene-polyisoprene diblock copolymers [8–10,12,15]. Under geometric confinements, the phase diagrams of diblock copolymers are clearly affected by the commensurability between the confined space size and the bulk structure period, and the surface fields. The one- and two-dimensional confined phase diagrams of diblock copolymers have also drawn considerable attention and have been intensively studied. Some investigations have concentrated on the confined phase diagrams of diblock copolymers and have provided a number of rational explanations [16–24]. Under confinement, the confined structures such as concentric lamellae, stacked disks/toroids, and so on, which are absent in bulk, have been identified using theories, simulations, and experiments [25–28]. When the number of dissimilar blocks

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increases from two to three, such as in ABC triblock copolymers, both the complexity and variety of self-assembled structures are significantly increased. In bulk, the phase diagrams of triblock copolymers are determined by at least five independent molecular structure/polymer parameters, namely, the two independent volume fractions  $f_A$  and  $f_B$  ( $f_C = 1 - f_A - f_B$ ), and the three interaction parameters  $\chi_{AB}N$ ,  $\chi_{BC}N$ , and  $\chi_{AC}N$ . A significant number of theories, simulations, and experiments have focused on the investigation of the bulk phase diagrams of triblock copolymers [29–37]. In particular, three-color flat lamellar phases are found to be the most stable when both the volume fractions and the interaction energies of the three species are comparable in the triangular phase diagrams. Moreover, core–shell hexagonal or tetragonal phases can be formed when one of the volume fractions is large. Two- or three-domain lamellae and hexagonally packed core–shell cylinders have also been verified in experiments through TEM using poly(styrene-*b*-isoprene-*b*-ethylene oxide) and poly(styrene-*b*-butadiene-*b*-methyl methacrylate) [12,38,39]. Furthermore, some complex morphologies, including lamellae containing beads, lamellae with beads at the interface, and hexagonal phases with beads at the interface, are also observed as the interaction energies between distinct blocks become asymmetric. These novel complex morphologies are obviously different from those observed in diblock copolymers and have superior mechanical attributes. Simultaneously, the bulk triblock copolymers are divided into non-frustrated (i.e., type  $F^0$ ) and frustrated (including types  $F^1$  and  $F^2$ ) systems according to the relative magnitude of  $\chi_{AC}N$  compared with those of  $\chi_{AB}N$  and  $\chi_{BC}N$  [40]. According to this dividing criterion, systems of the three categories (i.e., types  $F^0$ ,  $F^1$  and  $F^2$ ) have been characterized and corresponding triangular phase diagrams have also been well investigated [40–42].

Although many characteristics of ABC linear triblock copolymers in the bulk have emerged in the triangular phase diagrams, nanopore confinement can clearly elicit some new features. Nanopores possess curved surfaces on which chains can be rearranged. Thus, confined triangular phase diagrams can provide more opportunity to find some novel, special phase structures. Therefore, a systematic investigation of the confined triangular phase diagrams of triblock copolymers would be meaningful. However, previous investigations on triangular phase diagrams encountered some difficulties, such as the large complex parameter space and the limit in computational capability. Thus, to exhaustively search all possible points in the entire parameter space of triblock copolymers in a manner similar to that for AB diblocks would be impossible. Hence, we ignore the surface field of the ABC linear triblock copolymers and concentrate on the pure geometric effects. The present work aims to explore the characteristics of phase diagrams for ABC linear triblock copolymers confined in cylindrical nanopores. Self-consistent field theory (SCFT) calculation is used to investigate the characteristics of the ABC triblock copolymers in nanopores with suitable and invariant diameters. Similar to bulk melts, these confined triblock copolymers are also divided into three categories according to the relative magnitude of  $\chi_{AC}N$  compared with those of  $\chi_{AB}N$  and  $\chi_{BC}N$  in our paper. Thus, according to the Classification standard, we also roughly divide their corresponding confined triangular phase diagrams into the three categories, i.e., types  $F^0$ ,  $F^1$  and  $F^2$ . Morphologies with no A/C interfaces in the first category are observed, whereas the A/C interfaces dominate in the structures in the third category. The second category mainly favors the morphologies spanning a range of structures between those observed in the first and third categories. Lots of novel structures and characteristic features in the triangular phase diagrams of these three categories are then observed.

## 2. Theoretical method

A system of  $n$  incompressible ABC linear triblock copolymer melts confined in a cylindrical nanopore with diameter  $d/R_g$  and its volume  $V$  is investigated. The diameter is rescaled using the gyration radius  $R_g$  of an ideal Gaussian chain, and all spatial lengths in the calculations are expressed in  $R_g$  units. The ABC triblock copolymers are then regarded as Gaussian chains and assumed to be monodispersed with a degree of polymerization  $N$ . The chain lengths of the different A, B, and C chemically incompatible blocks are  $f_A N$ ,  $f_B N$ , and  $f_C N$ , respectively. The volume fractions of the three blocks are expressed in the equation,  $f_A + f_B + f_C = 1$ , where  $f_A$ ,  $f_B$ , and  $f_C$  are their corresponding volume fractions. Differences in the statistical segment lengths, i.e.,  $b_A = b_B = b_C = a$ , where  $a$  is the Kuhn segment length, are ignored. Within the field approximation based on the multi-chain Edwards theory, the free energy  $F/nk_B T$  of the  $n$  Gaussian triblock copolymer chains confined in a neutral cylindrical pore at a temperature  $T$  can be decomposed into two physically relevant contributions [9,11,43], namely,

$$\frac{F}{nk_B T} = \frac{U}{nk_B T} - \frac{S}{nk_B T} \quad (1)$$

with

$$\frac{U}{nk_B T} = \frac{1}{V} \int d\vec{r} [\chi_{AB} N \phi_A(\vec{r}) \phi_B(\vec{r}) + \chi_{BC} N \phi_B(\vec{r}) \phi_C(\vec{r}) + \chi_{AC} N \phi_A(\vec{r}) \phi_C(\vec{r})] \quad (2)$$

and

$$-\frac{S}{nk_B T} = -\frac{1}{V} \int d\vec{r} [W_A(\vec{r}) \phi_A(\vec{r}) + W_B(\vec{r}) \phi_B(\vec{r}) + W_C(\vec{r}) \phi_C(\vec{r})] - \ln \left( \frac{Q}{V} \right) \quad (3)$$

where  $U/nk_B T$  represents the internal energy per chain of the polymer–polymer interactions. In the confined melts, the spatial integration is restricted to the pore volume  $V$ . The interactions between the three dissimilar monomers are characterized by the three Flory–Huggins interaction parameters, namely,  $\chi_{AB}$ ,  $\chi_{BC}$ , and  $\chi_{AC}$ . In the present study,  $\phi_A(\vec{r})$ ,  $\phi_B(\vec{r})$ , and  $\phi_C(\vec{r})$  are the monomer densities of blocks A, B, and C, respectively. These densities are normalized by the local volume fractions of the blocks and are imposed with the incompressibility of the system by a Lagrange multiplier  $\epsilon(\vec{r})$ . In other SCFT calculations, the incompressibility constraint is set to be a step function [17] or a cosine function [44]. Recently, Meng and Wang [45] have suggested that the microstructures of equilibrium states are not significantly affected by the functional form of the incompressibility constraints. In the present work, we generalize the incompressibility constraint to be of the form

$$\phi_0(\vec{r}) = \sum_i \phi_i(\vec{r}) \quad (4)$$

where  $\phi_0(\vec{r}) = 1$  inside the cylindrical nanopore,  $\phi_0 = 0.5$  on the lattice near the boundary, and  $\phi_0 = 0$  on the boundary. These generalizations ensure the representation of an impenetrable boundary, resulting in the confinement of the triblock copolymers inside the cylindrical space. On the other hand,  $-S/nk_B T$  in Eq. (3) denotes the entropic free energy per chain from the chain stretching. The partition function  $Q$  is for a single chain in the mean chemical potential fields  $W_i(\vec{r}) = Nw_i(\vec{r})$  produced by the surrounding chains, where  $W_i(\vec{r})$  conjugates to  $\phi_i(\vec{r})$  and can be expressed in terms of the propagators  $q(\vec{r}, s)$  and conjugated  $q^+(\vec{r}, s)$ . The contour length is parameterized with a variable  $s$  that

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