Effect of Branching on Phase Behaviors of ABC Triblock Copolymers in Nonfrustrated Systems*

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Abstract—The phase behavior of linear dendritic triblock copolymer melts (AB$_2$C$_4$) is studied by self-consistent-field theory (SCFT) in order to find the effects of branching on the phase behavior of ABC linear triblock copolymer melts. We focus on a nonfrustrated systems in which $\chi_{NAB} = \chi_{NBC} = \chi_{NAC} = 40$ where A/C interface will not form. Frank-Kasper phases, asymmetric alternative sphere as well as traditional phases observed in diblock copolymer melts are found to be stable in the calculation.

I. INTRODUCTION

The phase behavior of AB diblock copolymer melts has been well studied in both SCFT simulation and experiments[1]. SCFT(Self-Consistent Field Theory) provides an efficient way to describe the phase behavior of block copolymer melts at equilibrium state. For the simplest AB diblock copolymer melts, the phase behavior is determined only by the volume fraction $f_A$ of the A block and $N$, the product of the chain length with Flory-Huggins parameter. By searching in a wide range of $f_A$ and $N$, FCC, BCC, Cylinder, Gyroid, Lamella, Fddd phases were proved to be stable[2]. Besides, other branching or asymmetric structures including AB$_2$ and AB$_4$ were studied. Two of the Frank-Kasper phases (A15[2], $\sigma$[3]) were stable on one side of the phase diagram and PL (perforated lamella) phase on the other side.

As for ABC triblock copolymer melts, the phase behavior is much more complicated. The phase behavior of a particular ABC triblock copolymer is determined by five parameters, the volume fraction $f_A$ of the A block, $f_B$ of the B block, the products $\chi_{NAB}$, $\chi_{NBC}$ and $\chi_{NAC}$ of the chain length with three different Flory-Huggins parameters. The huge parameter space leads to more sophisticated phases but also results in an impossibility in calculating all the possible circumstances. In order to make the calculation and analysis feasible, Bailey[4] came up with a method to divide triblock copolymers into three categories according to the relation of $\chi_{NAC}$ (the interaction between the two end blocks), $\chi_{NAB}$, and $\chi_{NBC}$. Bailey referred to nonfrustrated systems in which A/C interfaces are less thermodynamically expensive than A/B and B/C interfaces. In this kind of system, the relative position of the three blocks in formed phases are still in accordance with the topology of the molecule with no A/C interface formed. Core-shell structures, including core-shell spheres, cylinders, gyroid, lamellae and symmetric alternating structures, including alternating spheres (CsCl crystal), cylinders, gyroid, have been confirmed to be stable in nonfrustrated systems of ABC triblock copolymer melts[5].

However, the effects of branching on phase behavior have not been well studied in ABC triblock copolymers. We used a kind of linear dendritic triblock copolymer, AB$_2$C$_4$, where two B branches connect to the end of A block and two C branches connect to the end of each B branch. In our calculation, we only focus on nonfrustrated systems in which $\chi_{NAB} = \chi_{NBC} = \chi_{NAC} = 40$. The equality of these three parameters prevents the effect of frustration, thus the effects of branching in nonfrustrated systems can be independently analyzed. Since two of the three variables $f_A$, $f_B$, $f_C$ are independent because $f_A + f_B + f_C = 1$, we can use a ternary phase diagram to describe the phase behavior. On the three edges of this diagram, the triblock copolymer can be simplified into three kinds of diblock copolymers as Fig.1 shows. On the edge of $f_A = 0$, the copolymer can be regarded as C$_2$BC$_2$, whose phase behavior is similar to AB$_2$ diblock copolymer. On the edge of $f_B = 0$ and $f_C = 0$, the molecule is respectively equal to AC$_1$ and AB$_2$. The phase behavior on these three edges have all been well studied. Moreover, we can divide the phase diagram into three corners: A corner where C block forms a core surrounded by B shell in A matrix; C corner, where A block forms a core surrounded by B shell in C matrix; And B corner, where core-shell structures form on two sides and alternative phases form in the center. Special attention is paid to the Frank-Kasper phases and alternating phases in the calculation.

II. METHODOLOGY

The phase diagram is plotted by comparing the free energies of different candidate phases which have been proved stable or metastable in AB diblock copolymers and linear ABC triblock copolymers. The free energy is obtained from SCFT calculations using the pseudospectral method, combined with Anderson Mixing acceleration[6]. Twenty-one phases are calculated in our calculation. Since Frank-Kasper phases only appear at one side of the phase diagram in AB$_2$ and AB$_4$ copolymers, we only consider them in A corner and one side of B corner. Other Frank-Kasper phases, although not stable in both diblock copolymers and linear triblock copolymers, are also considered in these positions. All the candidate phases we have considered is shown in TABLE I.

III. RESULTS

In general, the phase behavior is determined by the competition of two factors, entropy and enthalpy. Interface energy, which means the interaction between differ-
red colors are respectively refer to A, B, C three blocks.

Fig. 1. The topology structure of $AB_2C_4$ in our calculation and its three extreme conditions on the three edges of the phase diagram. The blue, green, red colors are respectively refer to A, B, C three blocks.

**TABLE I**

| Phase | Space Group | Description |
|-------|-------------|-------------|
| $D$   |             | disorder    |
| $L$   |             | lamella     |
| BCC   | $Im3m$     | body-centered sphere |
| FCC   | $Fm3m$     | face-centered sphere |
| $C$   | $p6m$      | hexagonally packed cylinder |
| $G$   | $Ia3m$     | double-gyroid network |
| $A15$ | $Pm3m$     | Frank-Kasper phase |
| $\sigma$ | $P4_2/mnm$ | Frank-Kasper phase |
| C14   | $P63/mmc$  | Frank-Kasper phase |
| C15   | $Fm\overline{3}m$ | Frank-Kasper phase |
| C36   | $P63/mmc$  | Frank-Kasper phase |
| $Z$   | $P6/mmm$   | Frank-Kasper phase |
| $PL$  | $P6_3/mmc$ | perforated lamella |
| $Ga$  | $I4_132$   | alternating gyroid network |
| $CuCl$ | $Pm\overline{3}m$ | alternating sphere |
| $AlB_2$ | $P6/mmm$  | alternating sphere |
| $NaCl$ | $Fm\overline{3}m$ | alternating sphere |
| $Li_3Bi$ | $Fm\overline{3}m$ | alternating sphere |
| $S_{24,4}$ | $Im3m$   | alternating sphere |
| $C_{4,4}$ | $P4mm$   | alternating cylinder |
| $C_{6,3}$ | $P6mm$   | alternating cylinder |

At the C corner, the conformation asymmetry reshapes the phase behavior. In order to minimize the total stretching energy, a higher curvature of the interfaces is preferred. In this way, larger spherical phase can be stable instead of cylinders at a relatively large $f_A$, where the domains are largely shaped by the Voronoi cells and its interface energy increases as the surface are of the domain increases. Thus $\sigma$ and $A15$ phases should be stable here because they have larger average number of faces than BCC, which leads to lower interface energy. As a result, a phase sequence of $D-FCC-BCC-\sigma-A15(only \ on \ one \ side)-C-G-L$ occurs. Considering the Voronoi cells of $A15$ and $\sigma$ phases, the average number of faces in $A15$ phase is a little bit higher than that in $\sigma$ phase[3]. This means that the shape of Voronoi cells in $A15$ phase is closer to sphere, leading to a lower interface energy; on the other hand, $\sigma$ phase has a more uniform matrix which means a lower stretching energy. As a result, the $A15$ phase becomes stable when $\chi N$ is higher so interface energy plays a more important role, and when the volume of sphere is larger so stretching energy is less essential. However, as we can see on the right side of the phase region, $\sigma$ phase becomes stable again as $f_B$ increases from 0 and then diminishes, thus forming an isolated region. In order to explain this inconsistency, interface energy should be taken into consideration. When $f_B = 0$, the interface energy of $A15$ phase is lower than that of $\sigma$ phase, which makes $A15$ phase stable at the edge. As $f_B$ increases, the interface energy of $A15$ phase increases faster than $\sigma$ phase, leading to the stability of $\sigma$ phase. After the interface energy of $A15$ phase slows down its increase and becomes lower than $\sigma$ phase, $A15$ phase becomes stable again. Finally, when $f_B$ is relatively large, the gap of stretching energy between $A15$ phase and $\sigma$ phase grows too large to be compensated by the advantage of interface energy of $A15$ phase, and $\sigma$ phase returns stable. This process is shown in Fig.3.

In addition, we also considered several other Frank-Kasper...
phases including C14, C15, C36 and Z. However, none of these phases has an opportunity to be stable. The C14 and C15 phases can be stable in a binary blend system of diblock copolymers in which the two copolymer have different lengths of minority blocks. The C14 and C15 phases are tended to be stable when the ratio of the length of the longer chain over that of the shorter chain is relatively large so that the system can produce domains of different sizes[7]. The volumes of the different Voronoi cells in σ phase are 8.3292, 9.7126, 8.5605, 9.3564 and 9.1543(with a unit value of $R_g$), with 8.8855 and 9.1698 in A15 phase. However, the volumes are 8.3097, 8.3106 and 10.2175 in C14 phase, with 8.3144, 8.9514 and 10.2253 in C15 phase, and 8.1185, 9.2151 and 10.1413 in Z phase. These volumes are found in a SCFT calculation at $f_A = 0.15, \chi N = 40, b_A/b_B = 2.0$.[8] Although these phases may have a relatively lower interface energy than σ and A15 phases, their distinctive size of domains reflects a larger stretching energy therefore keeping them away from stable. However, in experimental condition, we cannot prevent the polymer chains diversify in degree of polymerization, so other Frank-Kasper phases can be stable in experiments instead of σ and A15 phases[7].

It should also be noticed that, as shown in Fig.4, on the right side of C corner, increasing $f_B$ has a similar effect on the phase behavior of triblock copolymer system comparing to the decrease of $\chi N$ in the corresponding diblock copolymer melts. If we start from a $AC_4$ diblock copolymer and increase $f_B$ while keeping $f_A$ fixed, it can be observed that BCC, FCC, A15 and σ phases diminish and disappear and then BCC phase appears again. Likely, if we decrease $\chi N$ from 40 in $AC_4$ diblock copolymer system, we can observe almost a same phenomenon[3] for sphere phases. This similarity can be seen in Fig.5. This similarity can be explained by tracing the volume fraction distribution in the interfaces. When $\chi N$ is reducing, the interface energy gets less important competing to the stretching energy so the interface is expected to be thicker, in other words, the gradient of volume fraction decrease in the interface. Therefore, the entropy is optimized with a cost of a small increase in interface energy. Now consider adding B clock and keeping $f_A$ fixed in $AB_2C_4$. Since $f_A$ remains unchanged, the volume fraction of A block remains unchanged in the A/C interface, but the volume fraction of C block decreases, leading to the decrease of gradient on the surface. As a result, it plays a similar role as reducing $\chi N$ in affecting the phase behavior.

When it comes to corner, the matrix on the two sides are different. On the edge of $AB_2$, C domain gradually forms in the center of the B matrix as $f_C$ increases. On the other edge of $B_2C_4$, A domain forms in the center of the C matrix as $f_A$ increases. However, these two patterns are not equally preferred. As discussed before, larger domains can be formed at a very small $f_C$ as long as C forms the matrix. So that C block is more preferred to form the matrix and only when $f_A$ is really small will B block form the matrix. B blocks are also expected to form the matrix when $f_A$ and $f_C$ are both large enough to form two independently alternating domains. However, in our calculation, there is no phase transition between core-shell phases and alternating phases. Firstly, a transition from FCC phase to NaCl and Li$_3$Bi phases is observed without a first order phase transition. The free energy, size of one unit cell and maximum volume fraction at the center of the domain are all smooth. When $f_C$ increases, the C domains are more likely to aggregate in the cavities among A domains. Positions with a larger CN (coordination number), where there is a larger cavity, are more preferred by the C blocks to fill in in order to minimize the interfacial energy. In FCC phase, there are two types of positions with $CN = 4$ and $CN = 6$ for C block to aggregate. In the process of increasing $f_C$, the positions with $CN = 6$ are firstly filled in by C blocks and NaCl phase forms; then the positions with $CN = 4$ are also filled in and Li$_3$Bi phase forms. These three phases have exactly the same space group. As $f_C$ continues increasing, the C domains connect to each other and form a matrix. Second, for BCC phase, the C block fills in at the positions with $CN = 4$ to form a $S_{24,4}$ phase, where A domain has a $CN$ of 24 and C domain has a $CN$ of 4. Thirdly, for C phase, the C block fills in the positions with $CN = 3$ to produce a $C_{6,3}$ phase. It also has to be qualified that this kind of aggregation does not mean that the C block concentrates in these positions. Instead, it seems like that B and C blocks together form the matrix and the volume fraction of C block is relatively higher in the cavities. Also, inside the C domains, the C block does not dominate the position. The volume fraction of B block is still high there, at least in the same order of magnitude as the volume fraction of C block. The distribution of the volume fraction of C block in BCC and $C_{6,3}$ is shown in Fig.6. This kind of phenomenon has some contradictions to ABC linear copolymers. In ABC linear copolymers system, where A and C blocks are symmetric, CsCl and $C_{4,4}$ phases are proved to be stable since A and C blocks can be regarded as equal in these two phases. A deeper study by Xie found that the difference between $CN$ of A and C domains increases as degree of asymmetry increases. Since the ratio of the $CN$(average coordination number) of C block to the CN of A block increases from 1 in NaCl, 1.15 in Li$_3$Bi to 6 in $S_{24,4}$ and all of them are not less than 1, we can attribute this phenomenon to the effects of branching, which makes A domain larger than C domain and $CN$ of A block larger than that of C block.

From this perspective, it can be noted that the alternating phases in our system are corresponded to core-shell phases as shown in TABLE II. The alternating phases formed by filling C block in the cavities among A domains of core-shell phases. The highly symmetric alternating phases(with a same $CN$ for A and C domains), including CsCl and $C_{4,4}$, which are corresponded to some metastable phases, PS(simple cubic spheres) and $C_4$(square array of cylinders), are proved to be dominant in linear ABC diblock copolymer melts because of their advantage in entropy, since there are more possibility for A or C block to disperse into more domains. However, in a highly asymmetric system,
different sizes of A and C domains diminishes this entropy advantage because of the highly nonuniform B matrix. As a result, alternating phases with different $CNs$ for A and C domains are preferred in an asymmetric system. Similarly, the alternating gyroid phase, which is a highly symmetric phase, are proved to be metastable in a branching system because the stretching energy of B domains increases observably.

Moreover, there is a abnormal transition of $BCC – FCC – BCC$ on one side of B corner as Fig.7 shows. In $AB_2$ system, it has been confirmed that a phase sequence of $FCC – BCC – σ$ occurs as $f_A$ increases. However, as $f_C$ grows larger, the matrix in $BCC$ and $σ$ phases are more uniform than that in $FCC$ phase, producing fewer cavities among A domains for the C domains to fill in and reducing the interface energy. Therefore, $FCC$ phase becomes a dominant sphere phase here. However, if $f_C$ continues increasing, C domains tend to connect to each other to become a matrix. In this circumstance, $BCC$, which has the most uniform matrix, becomes stable again.

**IV. CONCLUSIONS**

In summary, we have used SCFT to study the phase behavior of linear dendritic triblock copolymer melts ($AB_2C_4$). Nonfrustrated system is focused on with $\chi N_{AB} = \chi N_{BC} = 40$. Core-shell phases, including $FCC$, $BCC$, $A15$, $σ$, $C$, $G$, $L$, as well as alternating phases, including $NaCl$, $Li_3Bi$, $S_{24.4}$, $C_{6.3}$, has been proved stable. At C corner of the phase diagram, a phase sequence of $DFCCBCCσA15$ occurs on one side. The conformation asymmetry affects the phase behavior, since the curvature of the interfaces plays a more important role, therefore $σ$ and $A15$ becomes stable comparing to traditional spheres due to their advantages in interface energy. As $fB$ increases from 0, $σ$ phase becomes stable and forms an isolated region inside A1 phase region, which can also be explained by the difference of interface energy between $σ$ and $A15$ phase. Moreover, other Frank-Kasper phases have been proved metastable though they may have a lower interface energy than $A15$ and $σ$. This is mainly because their distinct sizes of Voronoi cells lead to a relatively higher stretching energy. On the right side of C corner, increasing $f_B$ seems to have a similar effect on the phase behavior comparing to reducing $\chi N$ in a corresponding diblock system, which is mainly due to their consistence in decreasing the gradient of volume fraction of each blocks on the A/C interface. Though alternating phases are found in our calculation, there is no first-order phase transition between core-shell phases and alternating phases. The transition process is the gradually aggregation of C blocks inside the cavities between A domains. $CN$(coordination number) is proved to be the key factor to the positions of C domains. Positions with a larger $CN$ is preferred for C block to fill in in order to minimize the interface energy. Unlike other traditional phases, this kind of aggregation is not equal to concentration, since B block is still high in those positions, which seems like B and C blocks together form the matrix. So from this aspect, the core-shell phases are corresponded to alternating phases in this system. Comparing to those symmetric alternating phases in linear ABC triblock copolymer system, alternating phases with different $CNs$ for A and C domains are preferred in asymmetric system due to the effect of branching.

**APPENDIX**

**ACKNOWLEDGMENT**

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