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Self-assembly of linear-dendritic triblock copolymer dependent on variant generations

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A B S T R A C T

A systematical calculation is performed to explore the equilibrium phase behaviors of linear-dendritic triblock copolymer $AB_{(2^{g+1}-2)}C_{2^{g+1}}$ (g is the generation number of the block B, and Gg is short for $AB_{(2^{g+1}-2)}C_{2^{g+1}}$) from G1 to G5 by using self-consistent field theory. Eight phases are found: two-colored lamellar phase, three-colored lamellar phase, hexagonal phase, core shell hexagonal phase, tetragonal phase, core shell tetragonal phase, two interpenetrating tetragonal phase, lamellar phase with beads except disordered phase, by varying the interaction parameters between different blocks, the volume fractions of the blocks and the generation number. While investigating the effect of linear coil length on morphology, we find the longer linear length ($f_A = 0.5$) for G1, G2 can be beneficial to form the lamellar phase, however, tend to form hexagonal phase easily with generation number increasing from 3 to 5, and short linear length ($f_A = 0.2$) can be better for inducing hexagonal phase from G1 to G5. It becomes more and more difficult to phase separate with generation number increasing from 1 to 5 due to the architectural complexity. However, increasing the interaction parameters is helpful to facilitate phase separation. It is likely to offer new opportunity for designing nanomaterials and applying to template technology by finely controlling the dendron generations, length of the linear chain, interaction parameters of linear-dendritic triblock copolymers.

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1. Introduction

Self-assembly of supramolecular polymers is providing infinite possibilities for technological advancements as supramolecular interaction, the architecture of macromolecular template and the diversity of side-groups attached to the polymer backbone are extensively explored [1–6]. In addition, it is a powerful tool for preparing functional materials of multiple properties, such as proton conductivity, anisotropic properties, and response to external conditions [6]. Dendritic supramolecular polymers, mainly based on amino-terminated polypropyleneimine (PPI-$(NH_2)_n$) or polyamidoamine (PAMAM-$(NH_2)_n$) [7–10], polyether [11–13] and carbosilane dendrimers [14,15], due to their highly efficient reactivity, have played an essential role in constructing novel liquid crystalline dendrimers.

Linear-dendritic block copolymers (LDBCs) representing a novel

macromolecular architecture were first proposed by Fréchet and Gitsov who had also investigated their drug load, delivery and therapeutic applications by varying the generation number of the dendrons and the length of the linear coil poly(ethylene oxide) (PEO) chains [16–18]. Then many experimental researchers have been directed towards their thermal behavior, and self-assembled structure and technical applications in solution [19–22] or in the bulk [23–26]. Usually, the first three generations of LDBCs were relatively easily prepared and intensively studied [11,12,27–29], but the higher generations were difficult to investigate. However, a few examples of great progress have been reported in LDBCs of higher generation number [7–10,30]. Even some more complex copolymers like dendritic-linear-dendritic and dendritic-linear-brush triblock copolymers have been well synthesized with some significant applications [31–36]. Over the past decades, LDBCs containing hydrophilic PEO or poly(ethylene glycol) (PEG) linear coils and hydrophobic crystalline alkyl chains on the periphery of the dendron have shown well-defined self-assembled behaviors in bulk [11,12,37–40]. Shi et al. [41,42] prepared a series of LDBCs combining linear PEG and dendritic PAMAM with functionalized

photoactive azobenzene mesogenic units bearing long alkyl tails at the periphery and systematically explored the phase behaviors and self-assembled structures of these liquid crystalline LDBCs in the bulk state as well as their photo-responsive properties and rich assembled morphologies in solution.

In general, the morphologies of supramolecular self-assembly and their applications are closely related, therefore, it is of great importance for various practical applications to well control the morphologies of the self-assembled structures. Although theoretical studies can provide molecular level insights to have a good knowledge of phase morphologies of complex polymers, so far few theoretical simulation studies focus on the phase behavior of LDBCs owing to the architectural complexity of these copolymers. Lee et al. [43] studied the equilibrium phase morphologies of two different dendritic block copolymer melts (G1 and G2) and found columnar square, rectangular and hexagonally packed structures by self-consistent mean-field theory. Mezzenga and coworkers [44,45] studied the self-assembly of a dendritic macromolecular system formed by a second-generation dendron with pH-responsive end groups and with a polymer chain emanating from its focal point in theory and experiment and then found hierarchical "inverted" hexagonal or lamellar structures as a result of their low volume fraction and the favorable entropy of the short alkyl tails confined within the cylinders. Usually it is difficult to investigate systematic morphologies of complex block copolymers because of the large experimental parameters space containing architecture, block compositions, temperature and molecule weights, thus it is comparatively laborious to explore [46]. Therefore, theory will probably play a more important role in guiding experiments as more chemists pay more attention to more complex block copolymers.

Herein we are inspired by the experimental study of Chen and coworkers [41] and apply self-consistent field theory (SCFT) to study the phase behavior of the linear-dendritic triblock copolymer $AB_{(2^{g+1}-2)}C_{2^{g+1}}$, which is widely adopted to predicting phase separation of block copolymer in solution [47–51] or in thin film [52–55] besides in melt. The structural model used in the simulation is the same as the experimental one above. For simplicity, the anisotropic interactions between mesogenic units are not considered. The triangle phase diagrams are constructed in the whole range of copolymer composition to understand how their analogue dendritic blocks affect the phase behaviors for G1, G2 and G3. This work also explores the effect of the length of linear coil chain A and interaction parameters on the phase stability. By finely tuning the dendron generation, length of the linear chain, interaction parameters, linear-dendritic triblock copolymers provide new possibilities for nanostructural materials and template application [27–29].

2. SCFT method

We assume linear-dendritic triblock copolymer $AB_{(2^{g+1}-2)}C_{2^{g+1}}$ with polymerization N_{tot} in a total volume V available for the polymer system. The linear-dendritic triblock copolymer contains a linear coil block A and tail chains C on the dendron B periphery. Thus, the total degree of polymerization $N_{tot} = N_A + (2^{g+1}-2)N_B + 2^{g+1}N_C$ and the total chain length $N = N_A + gN_B + N_C$. Schematic molecule structures of linear-dendritic triblock copolymer $AB_{(2^{g+1}-2)}C_{2^{g+1}}$ ($g = 1, 2, 3$) are presented in Fig. 1 The red, green, blue are assigned to A, B, C blocks, respectively. The linear coil chains, the dendrons and the tail chains are supposed to be flexible with a statistical length a. Therefore, the average volume fractions of three different compositions are $f_A = N_A/N_{tot}$, $f_B = (2^{g+1}-2)N_B/N_{tot}$, $f_C = 1 - f_A - f_B$ for A, B, C blocks, respectively.

The polymer segment probability distribution function in mean-
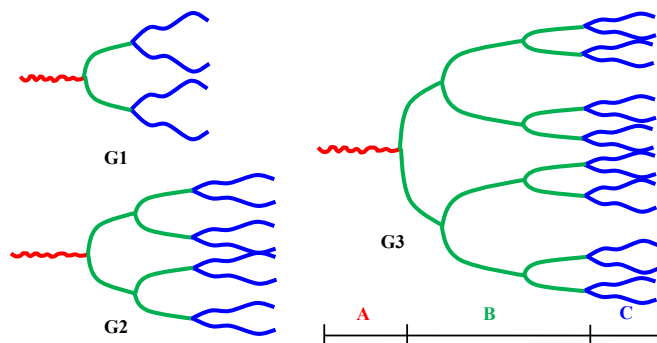

Fig. 1. Schematic molecular structures of linear-dendritic triblock copolymer $AB_{(2^{g+1}-2)}C_{2^{g+1}}$ ($g = 1, 2, 3$), referring to G1, G2, and G3 structures. The red, green, blue are assigned to A, B, C blocks, respectively.

field studies is the fundamental quantity to be calculated, representing the probability of finding segment s at position $\mathbf{r}$ and satisfying the modified diffusion equation with a flexible Gaussian chain model. With the different architectures of the blocks A, B and C, we define six distribution functions, i.e., $q_A(\mathbf{r}, s)$, $q_A^+(\mathbf{r}, s)$, $q_B(\mathbf{r}, s, t)$ and $q_B^+(\mathbf{r}, s, t)$, $q_C(\mathbf{r}, s)$ and $q_C^+(\mathbf{r}, s)$ where s is the contour along the coil chain for A and along the dendron B and end chains for C, t is the number along the block B divided by dendritic sites and it belongs to $[1, g]$. With these definitions, the polymer segment probability distributions q and q^+ for linear coil A, dendritic part B and the tails C satisfy the modified diffusion equations:

$$\frac{\partial}{\partial s}q = \frac{Na^2}{6}\nabla^2 q - wq \tag{1}$$

$$\frac{\partial}{\partial s}q^+ = -\frac{Na^2}{6}\nabla^2 q^+ + wq^+ \tag{2}$$

where w is w_A when s belongs to block A, w_B when belongs to block B, and w_C when belongs to block C. The w_A, w_B, and w_C are the effective external field of blocks A, B, C, respectively, which represent the actual interactions between different components. These external fields are conjugated to the segment density fields ϕ_i of different blocks i. The initial conditions are $q_A(\mathbf{r}, 0) = 1$, $q_A^+(\mathbf{r}, 0) = [q_B^+(\mathbf{r}, N_B, 1)]^2$, $q_B(\mathbf{r}, 0, 1) = q_A(\mathbf{r}, N_A)q_B^+(\mathbf{r}, N_B, 1)$, $q_B(\mathbf{r}, 0, t) = q_B(\mathbf{r}, N_B, t-1)q_B^+(\mathbf{r}, N_B, t+1)$ for $t > 1$, $q_B^+(\mathbf{r}, 0, g) = [q_C(\mathbf{r}, N_C)]^2$, $q_B^+(\mathbf{r}, 0, t) = [q_B^+(\mathbf{r}, N_B, t+1)]^2$ for $t < g$, $q_C(\mathbf{r}, 0) = 1$, $q_C^+(\mathbf{r}, 0) = q_B(\mathbf{r}, N_B, g)q_C(\mathbf{r}, N_C)$, where $t \in [1, g]$. Accordingly, the partition function of a single chain subject to the mean field w_i, where i represents block species A, B and C, can be written as $Q = \int d\mathbf{r}q_C(\mathbf{r}, N_C)$.

With the above description, the free energy function (in units of k_BT) of the system is given by

$$F = -\ln(Q/V) + 1/V \int d\mathbf{r}\left[\sum_{i \neq j}\chi_{ij}N\phi_i\phi_j - \sum_i w_i\phi_i - \xi\left(1 - \sum_i \phi_i\right)\right] \tag{3}$$

where χ_{ij} is the Flory–Huggins interaction parameter between different species ($i, j = $ A, B, C, $i \neq j$), ϕ_i is the monomer density of each species ($i = $ A, B, C), and ξ is the Lagrange multiplier (as a pressure).

Minimization of the free energy to mean field, density and pressure, $\delta F/\delta w = \delta F/\delta \phi = \delta F/\delta \xi = 0$, leads to the following self-consistent field equations that describe the equilibrium state: