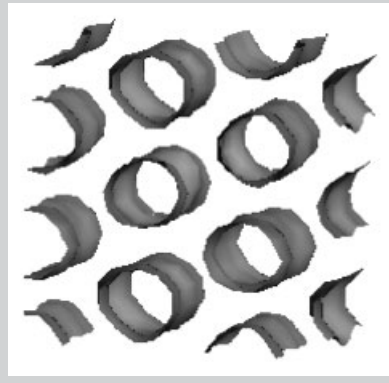
Summary: We used the dissipative particle dynamics method to simulate the self-assembly of symmetric triblock copolymers of the type ABA. Depending on the volume fraction of the end blocks f_A, several mesophases including lamellar, perforated lamellar, gyroid, hexagonal cylinders and bcc spherical micelles were obtained. The order-disorder transition (ODT) at $f_A = 0.5$ was found to be about $\chi N = 19.8$. The ODT for the cylindrical mesophase at symmetrical points on the phase diagram had different values, indicating asymmetry in the phase diagram. We were also able to estimate the bridge fraction in the different mesophases. They range from about 0.44 for the lamellar mesophase to about 0.75 for the spherical micelles. Our simulation results are in good agreement with previously reported theoretical calculations and experimental observations.



The hexagonal cylinders generated with the $A_6B_4A_6$ copolymer.

Morphology and Conformation Analysis of Self-Assembled Triblock Copolymer Melts

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Introduction

Self-assembly in block copolymers is a fascinating process in which copolymers undergo microphase separation into different ordered morphologies at the nano-meter scale. It happens as a result of the incompatibility between the different blocks composing the copolymer which is governed by the Flory-Huggins interaction parameter χ, the overall length of the copolymer N, and the volume fraction of each block f. Copolymers composed of A and B blocks with different architectures are recently given more attention by researchers for their potential applications.[1] In the field of nano-technologies and nano-materials, for example, they can be used as templates for the design of nano-devices. Also they are found to have good mechanical properties to be used as thermoplastics.

Nowadays, the thermodynamics and phase behavior of diblock copolymers is reasonably well understood.[2,3] Little attention, however, was given to more complex copolymers like the triblock copolymer. Matsen and Thompson[4] applied a self-consistent field theory (SCFT) to study the phase behavior of symmetric ABA triblock copolymer melts. They found that the phase diagram and the morphologies of the ABA triblock copolymers are very similar to those found for the AB diblock copolymer. Lamellar, gyroid, hexagonal cylinders and bcc (spherical micelles) mesophases were predicted. They noted however that the order-disorder transition (ODT) on the large side of end-block volume fraction (f_A) of the phase diagram and the locations of the phase boundaries were shifted and there were differences in domain spacing and interfacial widths when compared with the diblock copolymer. These findings were in agreement with some experimental observations[5–7] and other theories.[8,9]

As a consequence of the chain architecture of the ABA triblock copolymer, in a microphase-separated melt, a copolymer can have one of two different types of conformations: a loop or a bridge conformation. In the bridge conformation, the two ends of the ABA chain belong to two different A domains, while in the loop type the ends belong