The Effect of Synthetic Impurities on the Self Assembly of Cyclic Diblock Copolymers

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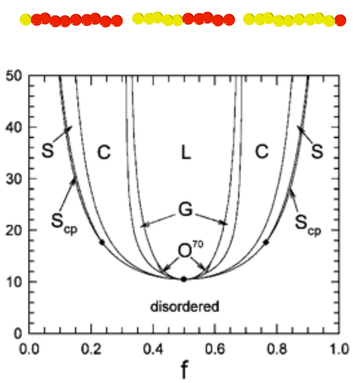
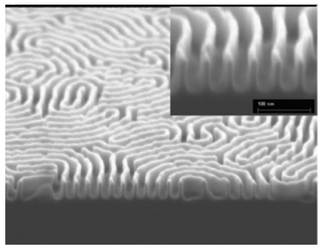
Abstract

Block copolymers (BCPs) are polymers consisting of two sections of different monomer chains. Due to their ability to self assemble, these molecules are being researched for a variety of applications. Cyclic BCPs have smaller domains than linear BCPs and therefore are being studied for their applications in nanolithography. Previous studies of cyclic BCPs have focused on pure systems. However, due to the difficulty of obtaining large amounts of pure cyclic BCPs, it is important to understand the effect that impurities have on nanostructure morphology and feature size.

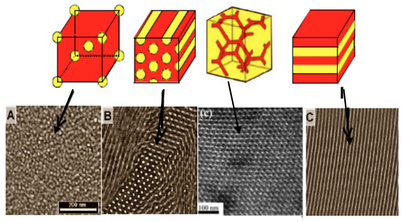
Block Copolymer Self Assembly

- Depending on chain length and composition, BCPs self assemble into several nanostructure morphologies[1] with a variety of applications.
- Cyclic BCPs exhibit 20-40% smaller domain spacing than their linear counterparts.[2]
- Cyclic BCPs are being studied for possible applications in nanolithography due to their reduced domain spacing.[3]





C. M. Bates, et. al., *Macromolecules*, 2013.



M.W. Matsen, *Macromolecules*, 2012.
M.C. Orilall and U. Wiesner, *Chemical Society Reviews*, 2011.
S.H. Lin, et. al. *Soft Matter*, 2012.

Synthesis and Impurities

- Synthesis of cyclic BCPs begins by preparing two linear homopolymer blocks.
- Click chemistry is used to connect the ends of the two homopolymer chains together.[2]
- Common impurities include linear diblock copolymers and linear homopolymer chains.

Methods

Dissipative Particle Dynamics (DPD)

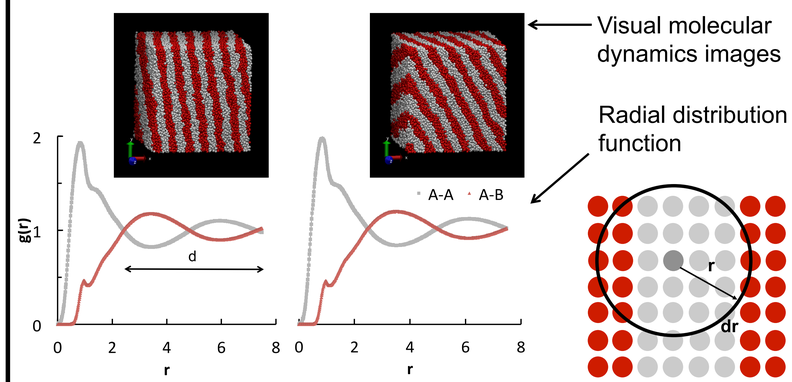
Coarse graining and soft repulsive forces allow DPD to simulate large systems over the long periods of time necessary for self assembly.

$$F_i = \sum_{j \neq i}\left(F_{ij}^C + F_{ij}^D + F_{ij}^R\right) + F_{ij}^S$$

$$F_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij})\widehat{r_{ij}} & (r_{ij} < r_c) \\ 0 & (r_{ii} \geq r_c) \end{cases}$$

$$\chi N = \frac{2\alpha(a_{ij} - a_{ii})(\rho_i + \rho_j)}{k_B T} N_{sim}$$

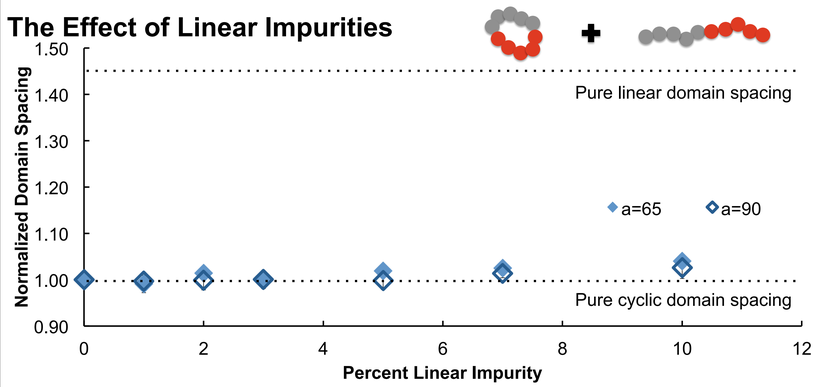
Determining Domain Spacing



Cyclic N=12, 1% Impurity Cyclic N=12, 10% Impurity

Results

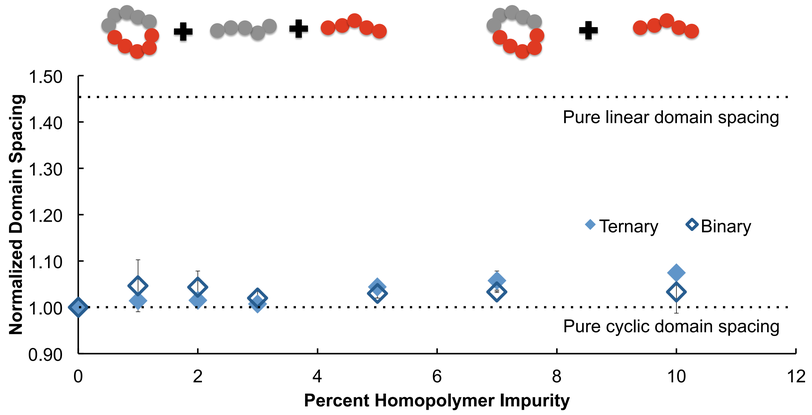
The Effect of Linear Impurities



The simulated polymers were 12 DPD beads long and had an a_{ij} (χ) parameter of 65 (solid) or 90 (open). Polymers with 8 and 16 DPD beads (not pictured) showed a similar trend. The domain spacings for each percentage were normalized to the pure cyclic domain spacing.

The Effect of Homopolymer Impurities

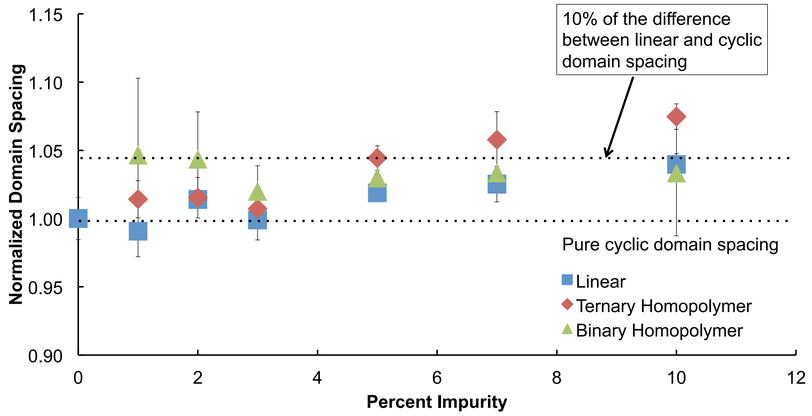
Two Homopolymer blends were studied:
1. Ternary (solid)
2. Binary (open)



The simulated polymers were 12 DPD beads long and had an a_{ij} (χ) parameter of 65.

Conclusions

- Previously, studies of cyclic BCP self assembly have assumed high purity is required. However, these simulations suggest that linear and homopolymer impurities have little effect on the morphology and domain spacing of cyclic BCPs in lamellar nanostructures.
- The simulations indicate that the domain spacing of lamellar nanostructures increases linearly with amount of linear BCP and homopolymer between 0% and 10% impurity. This increase is still within the margin of error associated with many experimental measurements.
- Future studies should analyze the effect of linear and homopolymer impurities on other nanostructure characteristics (e.g. interfacial roughness). Research is also needed on systems in thin films as these simulations are carried out in the bulk.



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Acknowledgements

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