The Effect of Additive Cyclic Blends on Linear Block Copolymer Domain Spacing

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Abstract

Block copolymers (BCPs) can be used as templates for nanolithography. Advancing technology demands smaller lithographic features. Cyclic BCPs have smaller features than their linear analogues but are difficult to synthesize in high purity. We use DPD simulation to investigate the potential of cyclic BCPs as an additive to shrink domain spacing of linear BCPs. We have found a strong linear relationship between cyclic content and reduced domain spacing. Additionally, adding an ordered cyclic BCP can induce order in an otherwise disordered linear BCP. This approach may allow for further shrinking of domain spacing, as lowering the parameters χ and N results in smaller features but potentially disordered systems.

Block Copolymer Self Assembly

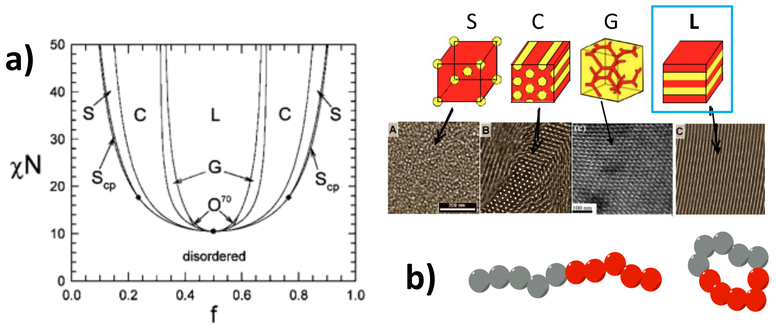


Figure 1:
Based on chain length and composition, block copolymers self assemble into nanoscale morphologies **(a)**[1,2] which have a variety of applications.
This work focuses on the lamellar (banded) morphology (**a**)[1,2]
Cyclic BCPs (**b**) form features 20-40% smaller than their linear analogues.

Application

- Block copolymers can be used for nanolithography. For the required scale, the width of the lamellar bands (feature size) must be as small as possible. One interesting way to reduce domain spacing is to use cyclic block copolymers instead of linear ones.
- Cyclic block copolymers are much more difficult to synthesize than linear ones.
- This research uses simulation to test the effectiveness of using cyclic block copolymer as an additive into linear block copolymers of similar composition to reduce domain spacing.

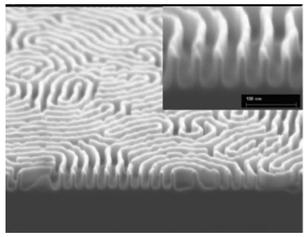


Figure 2[3]: A lamellar block copolymer with one polymer type removed

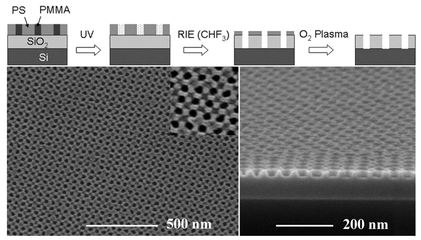
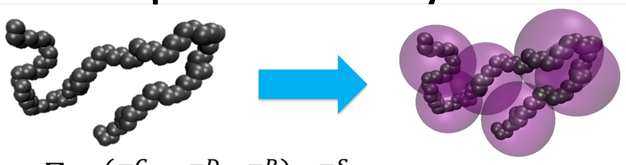


Figure 3[4]: The process of block copolymer nanolithography

Dissipative Particle Dynamics



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

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

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

Figure 4: Coarse graining allows DPD to simulate large systems over long periods of time[5].

Analysis Methods

Figure 5: Domain Spacings are measured using radial distribution functions.

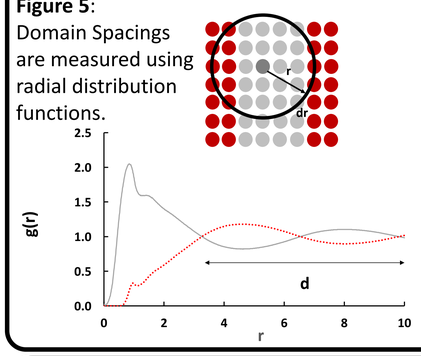
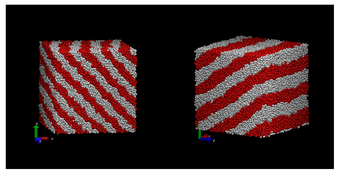


Figure 6: Visual Molecular Dynamics (VMD) is used to generate snapshots of the simulated polymers.



Cyclic-Linear Blend Domain Spacing

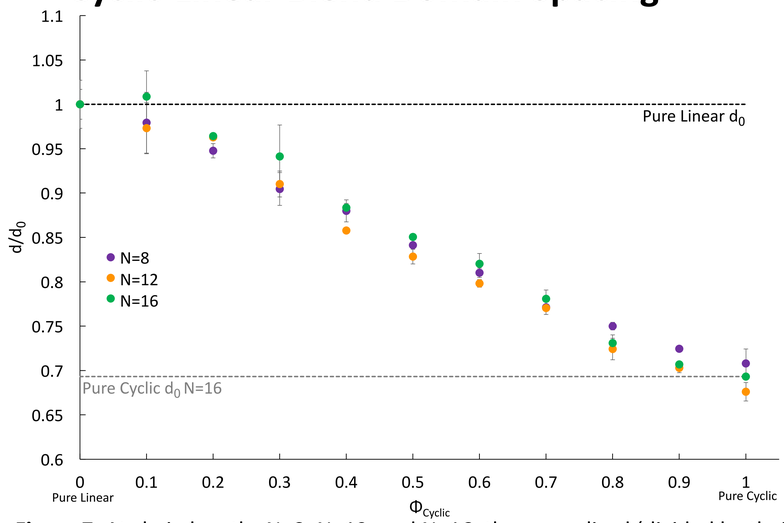


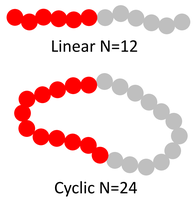
Figure 7: At chain lengths N=8, N=12, and N=16, the normalized (divided by their respective pure linear domain spacing) domain spacing has a strong linear relationship with percent cyclic BCP in the blend. For each simulation, a=65.

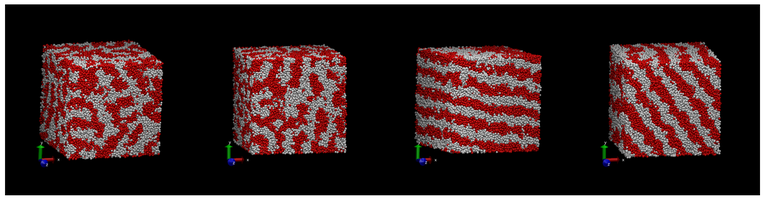
References

1. M.W. Matsen, *Macromolecules*, 2012.
2. M.G. Buonomenna, et. al. *RSC Adv.*, 2012.
3. C. M. Bates, et. al., *Macromolecules*, 2013.
4. C. Tang, C.J. Hawker, et. al. *Science*, 2008.
5. R.D. Groot and P.B. Warren, *J. Chem. Phys.*, 1997

Order-Disorder Transition (ODT)

- The order-disorder transition is the point (χN value) where a block copolymer transitions from a disordered state to an ordered one (see figure 1a).
- Low χN values correspond to lower domain spacing but may be below the ODT.
- Adding small amounts of ordered cyclic block copolymers to disordered linear block copolymers may induce order.





Pure Linear N=12 | 10% Cyclic Blend | 25% Cyclic Blend | Pure Cyclic N=24

Figure 8: Blends of linear N=12 + cyclic N=24 at a=35 (low χ) show a transition from disorder to lamellar between 10% cyclic and 25% cyclic.

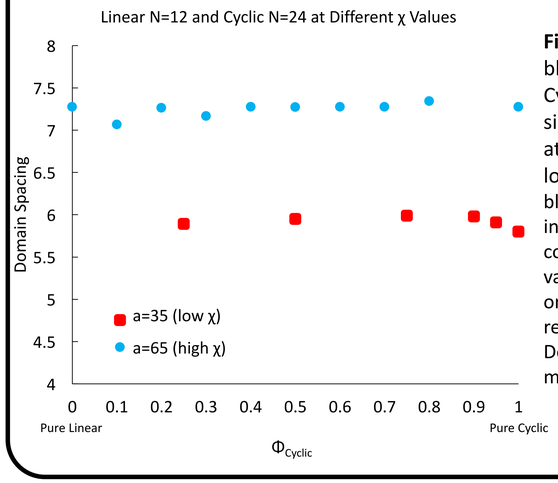


Figure 9: Comparison of blends of Linear N=12 and Cyclic N=24 (which have similar pure domain spacings) at different χ values. At the lower χ value, ordered cyclic block copolymers are blended into disordered linear block copolymers. At the higher χ value, both linear and cyclic are ordered. The lower χ value results in lower domain spacing. Domain spacings are only measured for ordered systems.

Conclusions and Future Work

- Blending cyclic block copolymers into their linear analogues reduces domain spacing linearly.
- Blending ordered cyclic block copolymers into disordered linear block copolymers can result in ordered systems. This represents a way to reduce domain spacing, as lower χ values and chain lengths correspond to lower domain spacing but may be below the ODT.
- More simulations of different χ values and chain lengths will be carried out to further test the effectiveness of cyclic-linear blends to induce order.
- Ultimately, thin film simulations are necessary, as nanolithography uses thin films (these simulations are in the bulk, but should not have crucial differences to thin film simulations). Cylinder simulations (see figure 1a) are another future possibility, as cylinders are also used for nanolithography.

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