Binary Mixtures of Diblock Copolymers: A New Route to Novel Bicontinuous Phases

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Cubic Bicontinuous Phases: Struts & Nodes

- **Struts**
  - Double Gyroid (G) (Ia3d)
  - Double Diamond (DD) (Pn3m)
  - Plumber's Nightmare (P) (Im3m)

- **Nodes**

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Problem: Packing Frustration
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Volume Difference between Struts and Nodes → Unequal Stretching of Chains → Packing Frustration

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Solution: Space-filling Additives
Solution: Space-filling Additives

Packing frustration can be reduced by including homopolymers to the blend [1-5].

The New Route?

**Task:** To examine the possibility of stabilizing the novel bicontinuous phases, such as the double-diamond or P morphology, in the case where the additive is a second species of diblock copolymer.

We focus on binary blends of:

**Gyroid-forming Species**

\[ f_\text{A} = 0.34 \]

**Homopolymer-like (HL) Chain**

\[ f_\text{A} = 0.95 \]

\[ N_\text{DBC} \]

\[ N_\text{HL} = \alpha N_\text{DBC} \]

Self-consistent field theory [1-3] is used to study to the resulting phase behavior.

Stabilization of the DD Phase

Gyroid-forming Species  +  Homopolymer-like (HL) Chain

$\chi_{AB} N_{DBC} = 25.$
Improved Stability of DD Phase

Stability region of the double-diamond phase spans \( \sim 10\% \) in the average additive concentration at \( \alpha = 2.32 \).
A-Majority Gyroid Phase

for an average A-monomer volume fraction, $\phi_A$, ranging from 45% to 60%!
Return to Homopolymers

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Gyroid-forming Species + Homopolymer

\( \chi_{AB} N_{DBC} = 25. \)
Early Macro-phase Separation

The inclusion of B monomers onto the additive is vital for stabilizing the double-diamond phase!
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The Stable P Morphology

Confinement to the Nodes

Gyroid-forming Species + Homopolymer-like (HL) Chain

G  DD  P  L  DIS
Confinement to the Nodes

**Fig. 6**) Plot of the volume fraction of the homopolymer-like chain, $\phi_{HL}$, as a function of the relative distance from the center of the node for a metastable P phase at $\bar{\phi}_{HL} = 0.4$. 

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>Color</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.4$</td>
<td>Red</td>
<td>$\alpha = 1.4$</td>
</tr>
<tr>
<td>$1.67$</td>
<td>Green</td>
<td>$\alpha = 1.67$</td>
</tr>
<tr>
<td>Interface - $\phi_A = 0.5$</td>
<td>Orange</td>
<td>Interface - $\phi_A = 0.5$</td>
</tr>
</tbody>
</table>
The observed behavior suggests that packing frustration is indeed relieved!
Examining the Mean Curvature

\[(a) \ H_{\text{min}} R_g = 0.155 \]

\[(b) \ H_{\text{min}} R_g = 0.130 \]

\[\alpha = 2.32, \text{ and } \chi_{AB} N_{DBC} = 25\]

Entropy-driven Curvature →
Entropy-driven Curvature

Melt incompressibility and maximization of conformational entropy
Flattening of the Interface

(a) $H_{\text{min}}R_g = 0.155$

(b) $H_{\text{min}}R_g = 0.130$

Encircled areas are slightly flatter for the homopolymer-like species, which increases the conformation entropy.
Segregation on the AB-Interface

Dual-Purpose Additives

16% HL Chains

Gyroid-forming Species
Dual-Purpose Additive

The homopolymer-like species serves two purposes:
(1) "Space" filler relieving packing frustration
(2) Flattens the interfacial curvature, making it more entropically favorable for the G-forming species
Recap

Using self-consistent field theory, we have showed in binary mixtures of diblock copolymers

- The stabilization of the double-diamond, and plumber's nightmare phase.
- The resulting stability regions of the novel bicontinuous phases can be extended by using homopolymer-like chains.

Gyroid-forming \( (f_A = 0.33) \)  +  Homopolymer-like \( (f_A = 0.95) \)
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Minimization of Interfacial Area

The system ideally wants to form a constant-mean-curvature structure in order to minimize the interfacial surface energy. This results in [1]

Strut volume < Node volume

With the least number of struts per node, 3, the G phase will experience smallest degree of packing frustration, explaining why is the sole representative for the cubic bicontinuous phases in monodispersed AB-diblock melts.
Methodology

Self-consistent field theory [1-3] is used to study the resulting phase behavior.

Basic idea:

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**Stabilization of the DD Phase**

Fig. 3) Phase diagram of diblock copolymers ($f_A = 0.33$) and a homopolymer-like species ($f_A = 0.05$) at different compositions of HL chains, $\varphi_{HL}$, and values of $\alpha$. The interaction strength is $\chi_{AB} N_{DBC} = 25$. The phases are labelled as follows: H for the cylindrical phase, G for the double gyroid phase, D for the double diamond phase, and DIS for the homogeneous phase.

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BONUS: Diamond → Gyroid Transition

as concentration of additives continues to increase for all studied values of $\alpha$

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A-Majority Gyroid Phase

for an average A-monomer volume fraction, $\bar{\phi}_A$, ranging from 45% to 60%! The G morphology only exists for $\bar{\phi}_{A,B} \approx 0.30$ to 0.35 in monodispersed melts [?].
**Fig. 3** Phase diagram of diblock copolymers ($f_A = 0.34$) and a homopolymer-like species ($f_A = 0.05$) at different compositions of HL chains, $\phi^{HL}$, and values of $\alpha$. The interaction strength is again $\chi_{AB} N_{DBC} = 25$. The lamellar phase is labelled as L.
An elaborate sequence of stable bicontinuous phases is found near $\chi_{AB} N_{DBC} \approx 23$ as the concentration of the additive species is increased, $G \rightarrow DD \rightarrow P \rightarrow DD \rightarrow G$. 
Pausing for a moment...

We have so far looked at the effects of the
  • Chain length ratio, $\alpha$
  • Volume concentration of the homopolymer-like species, $\phi^{\text{HL}}$
  • Segregation strength

Next part of the journey is to understand the formation of the novel bicontinuous phases arising from blending the homopolymer-like chains.