Non-Equilibrium Structures in Block Copolymers

Kink Bands
Lamellae Contraction
Solvent-Induced Morphologies

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Non-Equilibrium Structures in Block Copolymers

- **Kink bands**
  - Initiation
  - Dynamics of kink bands -- lamellar rotation mechanism
  - ASIDE: rotation of lamellae matrix
  - Termination -- boundary transformation
  - Relaxation -- focal conics

- **Lamellae contraction in parallel lamellae**
  - Molecular weight and shear rate dependence
  - Correlation with applied shear stress

- **Solvent-induced morphologies in Triblock Copolymers**
  - Selective solvents and morphological transitions

Kink Bands

**Diblock copolymers** (PS-PEP), poly(styrene-co-ethylene propylene)

**Intermediate to strong** segregation.

\[ \chi N = 35 \text{ to } 105 \] at 180°C

**Steady shear rate.**

Pre-aligned for **parallel orientation.**
**Forward Kink Band**

![Image](image.png)

Figure 1 a&b

SEP 40-70; FE-SEM of 1-2 plane; shear to right; Polis 1998

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**Initiation: Forward Kink Bands**

Residual defects in predominately parallel starting state.

![Image](image2.png)

**Starting State**

( LAOS )

$\gamma = 1$

(180°C, 0.001 s$^{-1}$)

SEP 40-70; TEM of 1-2 plane; shear to right; Qiao 2000
**Initiation: Forward Kink Bands**

- Addition of silica spheres increases the volume of kink bands.

![Graphs showing intensity vs. azimuthal angle](image)

SEP 38-62; SAXS of 1*-2* plane; 180C, 0.005 s⁻¹; Polis 1999

**Initiation: Forward Kink Bands**

- Residual defects in predominately parallel starting state.
- A critical strain amplitude (~40%) is required to produce a kink band.
- At lower strains an S-shaped defect is found.

**Starting State**

- \( \gamma = 0.3 \)

(180C, 0.05 s⁻¹)

SEP 40-70; FE-SEM of 1-2 plane; shear to right; Polis 1998
Initiation: Conjugate Kink Bands

As molded starting state
Large Amplitude Oscillatory Shear:
12h, 150C, g=40%, 1 s⁻¹

Figure 5, 4, 6

Dynamics: Forward Kink Bands

Lamellar rotation
- Lamellae inside k.b. rotate w/ strain
- Constant k.b. width

Boundary migration
- Lamellae orientation inside k.b. fixed
- Increasing k.b. width w/ strain

SEP 40-70; FE-SEM of 1-2 plane; Polis 1996
**In Situ SAXS - Rheology**

(Synchrotron 16.1, Daresbury Laboratory, UK.)

- SEP(38-62), 100 kg/mol, 38% PS.
- Oscillatory shear
- Steady shear: 0.001, 0.01, and 0.1 s⁻¹

**In situ SAXS-Rheology**

Starting State

\[ \gamma = 0 \]

TEM image after LAOS shows forward kink bands.

Starting State

\[ \gamma = 0 \]

SAXS pattern shows an asymmetric peak along the 2° direction.

SEP 38-62; SAXS of 1°-2° plane; 180C; Qiao 2001
Kink Bands in Block Copolymer Lamellar Phases

SEP 38-62; SAXS of 1*-2* plane; 180C; Qiao 2001
**Dynamics: Forward Kink Bands**

- $\mu_k \uparrow$ w/ strain suggests lamellar rotation
- Rate of rotation $\downarrow$ w/ strain
- Area under kink band peak $\sim$ constant

SEP 38-62; SAXS of 1°-2° plane; 180°C; Qiao 2001

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**Assumptions:**
- Idealized, well-defined kink bands in aligned layered matrix
- Homogeneous deformation across domains

**Predictions:**
- *Negligible tangential slip* for narrow boundaries — thus ruling out boundary migration mechanism
- Rate of rotation:
  $$ \mu = 2 \gamma \cos^2 (\mu/2) $$
Dynamics: Forward Kink Bands

For a given population of kink bands, the model predicts the development of kink bands with strain.

\[ \dot{\mu} = 2 \gamma \cos^2 \left( \frac{\mu}{2} \right) \]

Qualitative Agreement
- \( \mu_b \uparrow \) w/ strain suggests lamellar rotation
- Rate of rotation \( \downarrow \) w/ strain
- Area under kink band peak \( \sim \) constant

SEP 38-62; SAXS of 1*-2* plane; 180C; Qiao 2001
\[ \gamma = 0.1 \text{s}^{-1} \]

SEP 38-62; SAXS of 1*-2* plane; 180C; Qiao 2001
How do kink bands evolve w/ strain?

- Kink bands evolve through **lamellar rotation**, the rate of rotation follows:
  \[
  \dot{\mu} = 2 \gamma \cos^2 (\mu / 2)
  \]

- The predicted rate of rotation shows an **accurate fit at the highest shear rate**.
- Deviations at lower rates are presumably due to the presence of spontaneous **domain relaxation**.

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Dynamics: Forward Kink Bands

- Peak maximum moves in the anti-vorticity direction due to lamellae rotation and the consequent pile up.

SEP 38-62; SAXS of 1^*-2^* plane; 180C, 0.005 s⁻¹; Polis 1999
**Termination: Forward Kink Bands**

\( \gamma = 1 \)

Chevron boundary

\( \gamma = 3 \)

Omega boundary

SEP 40-70; TEM of 1-2 plane; 180°C, 0.001 s\(^{-1}\); Qiao 2000

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**Termination: Forward Kink Bands**

\( \gamma = 5 \)

Omega boundary

\( \gamma = 10 \)

Broken boundary

SEP 40-70; TEM of 1-2 plane; 180°C, 0.001 s\(^{-1}\); Qiao 2000
### Termination: Forward Kink Bands

**Tilt Angle vs. Strain**

SEP 40-70; TEM of 1-2 plane; 180C, 0.001 s⁻¹; Qiao 2000

### Quiescent Tilt Boundary


- **Chevron**
- **Intermediate**
- **Omega**

Self-consistent field theory predicts **boundary transformation with decreasing tilt angle.**

**Why?** Reduce: interfacial energy, bending energy, and overall packing frustration.
Kink Bands in Block Copolymer Lamellar Phases

**Evolution of Kink Bands and Tilt Boundaries in Block Copolymers at Large Strains**

- Kink bands persist at large strains, and evolve by **lamellar rotation** and **boundary transformation**.
- Upon increasing strain, kink band boundary transforms from *chevron* boundary to **various omega** boundaries to *broken* omega boundaries.
- **PS** domains are the **weaker** domains, contributing to the broken boundaries at large strains

**Relaxation: Conjugated Kink Bands**

- As molded starting state
- Large Amplitude Oscillatory Shear: 12h, 150°C, g=40%, 1 s⁻¹
- Anneal: 150°C, 2h

SEP 40-70; FE-SEM of 1-2 plane; Polis 1996
Relaxation: Conjugated Kink Bands

- As molded starting state
- Large Amplitude Oscillatory Shear: 12h, 150°C, g=40%, 1 s⁻¹
- Anneal: 150°C, 48h

- As molded starting state
- Large Amplitude Oscillatory Shear: 12h, 150°C, g=40%, 1 s⁻¹
- Anneal: 150°C, 168h

SEP 40-70; FE-SEM of 1-2 plane; Polis 1996
Lamellae Contraction

Alignment by oscillatory shear

In situ SAXS-Steady shear
\( \gamma(\text{max}) = 80\% \); 180° C, RAPID detector

<table>
<thead>
<tr>
<th>Materials</th>
<th>( D_s ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEP(39-24)</td>
<td>45</td>
</tr>
<tr>
<td>SEP(38-62)</td>
<td>70</td>
</tr>
<tr>
<td>SEP(111-83)</td>
<td>109</td>
</tr>
</tbody>
</table>

SEP; SAXS of 1*2* plane; 180C; Qiao 2002
Kink Bands in Block Copolymer Lamellar Phases

**SEP(111-83)**

- 0.001 s\(^{-1}\)
- 0.01 s\(^{-1}\)
- 0.1 s\(^{-1}\)

\[
\frac{D}{D_0} \sim \gamma
\]

\[
\sigma \sim \gamma
\]

**Steady shear @ 0.1 s\(^{-1}\)**

- SEP(39-24)
- SEP(38-62)
- SEP(111-83)
**Contraction: Chain Conformation Distortion**

- Lamellar spacing balances interfacial and stretching energy.
- Lamellar contraction requires distortion of chain conformation.
- As shear rate $\uparrow$  \Rightarrow Less relaxation and less strain dissipation  
  \Rightarrow More distortion, more contraction
- As molecular wt $\uparrow$  \Rightarrow entanglements $\uparrow$, more distortion $\uparrow$  
  \Rightarrow More distortion, more contraction

**Constraints on Morphology:**

Area per junction must be the same for both blocks  
Stress should be approximately uniform perpendicular to the lamellae  
Strain can vary perpendicular to the lamellae and even within a microdomain. This can lead to different amounts of contraction in the A and B microdomains.

**Contraction vs. Shear Stress**

The amount of lamellar contraction depends on the applied shear stress, which is influenced by either molecular weight or shear rate.
**Contraction, stress and modulus:**

**Assumption:**
- Elastic distortion
- Constant stress, uniform strain across lamellae

**Prediction:** \( \frac{D-D_0}{D_0} \sim \sigma^2/(\sigma^2+3G^2) \)
Solvent-Induced Non-Equilibrium Morphologies

<table>
<thead>
<tr>
<th>Solvent</th>
<th>δ (MPa$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene (PS)</td>
<td>19.0</td>
</tr>
<tr>
<td>Polysisoprene (PI)</td>
<td>15.1</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>16.8</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.5</td>
</tr>
<tr>
<td>Dioxane</td>
<td>20.3</td>
</tr>
</tbody>
</table>

**Solvent-casting** (in air, 3 weeks; in vacuum, 80°C, 48hr)

Morphological characterization (TEM, SAXS) and mechanical testing (E).
Kink Bands in Block Copolymer Lamellar Phases

**67-ISI, as-cast**

![Graph showing scattering data for different solvents](image)

Cyclohexane  | Toluene  | Dioxane

**After annealing: equilibrium structure**

**38-ISI**
- Gyroid

![Graph showing scattering data for gyroid structure](image)

**67-ISI**
- Lamellae

![Graph showing scattering data for lamellar structure](image)
**As-cast** → **Annealed**

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility parameter, $\delta$ (MPa$^{1/2}$)</th>
<th>38-ISI</th>
<th>52-ISI</th>
<th>67-ISI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexane</td>
<td>16.8</td>
<td>C → G</td>
<td>L → L</td>
<td>L → L</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.5</td>
<td>G → G</td>
<td>L → L</td>
<td>L → L</td>
</tr>
<tr>
<td>Dioxane</td>
<td>20.3</td>
<td>L → G</td>
<td>L → L</td>
<td>C → L</td>
</tr>
</tbody>
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<tr>
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<td>16.8</td>
<td>C → L</td>
<td>L → L</td>
<td>L → C</td>
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<tr>
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<td>L → L</td>
<td>L → L</td>
<td>C → C</td>
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<tr>
<td>Dioxane</td>
<td>20.3</td>
<td>L → L</td>
<td>L → L</td>
<td>C → C</td>
</tr>
</tbody>
</table>

**Area per Junction**

- Area per junction larger in as-cast samples.
- Effect of solvent is influenced by the solubility parameter and evaporation rate.
Kink Bands in Block Copolymer Lamellar Phases

**Modulus vs. As-Cast Morphology, chain architecture**

<table>
<thead>
<tr>
<th>$\phi_s$ (%)</th>
<th>Solvent</th>
<th>Morphology</th>
<th>SIS (ksi)</th>
<th>ISI (ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>38</td>
<td>Cyclohexane</td>
<td>C</td>
<td>10.1</td>
<td>5.4</td>
</tr>
<tr>
<td>38</td>
<td>Toluene</td>
<td>G</td>
<td>—</td>
<td>14.0</td>
</tr>
<tr>
<td>38</td>
<td>Toluene</td>
<td>L</td>
<td>19.8</td>
<td>—</td>
</tr>
<tr>
<td>38</td>
<td>Dioxane</td>
<td>L</td>
<td>21.0</td>
<td>7.8</td>
</tr>
<tr>
<td>52</td>
<td>Toluene</td>
<td>L</td>
<td>21.2</td>
<td>17.8</td>
</tr>
<tr>
<td>52</td>
<td>Dioxane</td>
<td>L</td>
<td>32.6</td>
<td>22.2</td>
</tr>
<tr>
<td>67</td>
<td>Toluene</td>
<td>C</td>
<td>102.9</td>
<td>—</td>
</tr>
<tr>
<td>67</td>
<td>Toluene</td>
<td>L</td>
<td>—</td>
<td>34.3</td>
</tr>
<tr>
<td>67</td>
<td>Dioxane</td>
<td>C</td>
<td>73.2</td>
<td>42.3</td>
</tr>
</tbody>
</table>

- $E \uparrow$ with $\phi_s$: 38-SIS < 52-SIS < 67-SIS.
- $E \uparrow$ with domain connectivity:
  - PS cylinders < Lamellae < Double Gyroid.
  - Lamellae < PI cylinders.
- $E \uparrow$ with trapped entanglements: SIS > ISI.