

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

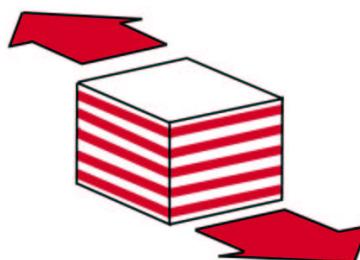
Kink Bands

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

Intermediate to strong segregation.
 $\chi N = 35$ to 105 at 180°C

Steady shear rate.

Pre-aligned for parallel orientation.



Kink Bands in Block Copolymer Lamellar Phases

Forward Kink Band

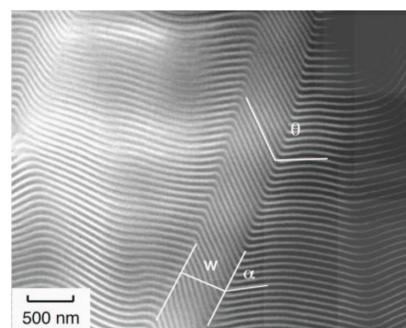
Figure 1 a&b

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

Initiation: Forward Kink Bands

Residual defects in predominately parallel starting state.

Fig. 1



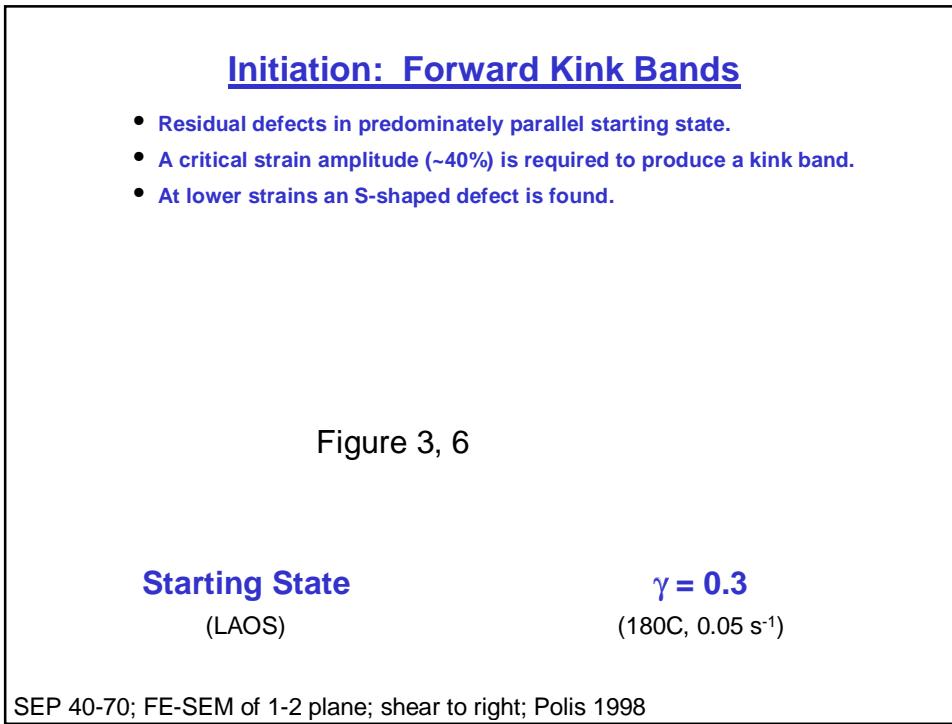
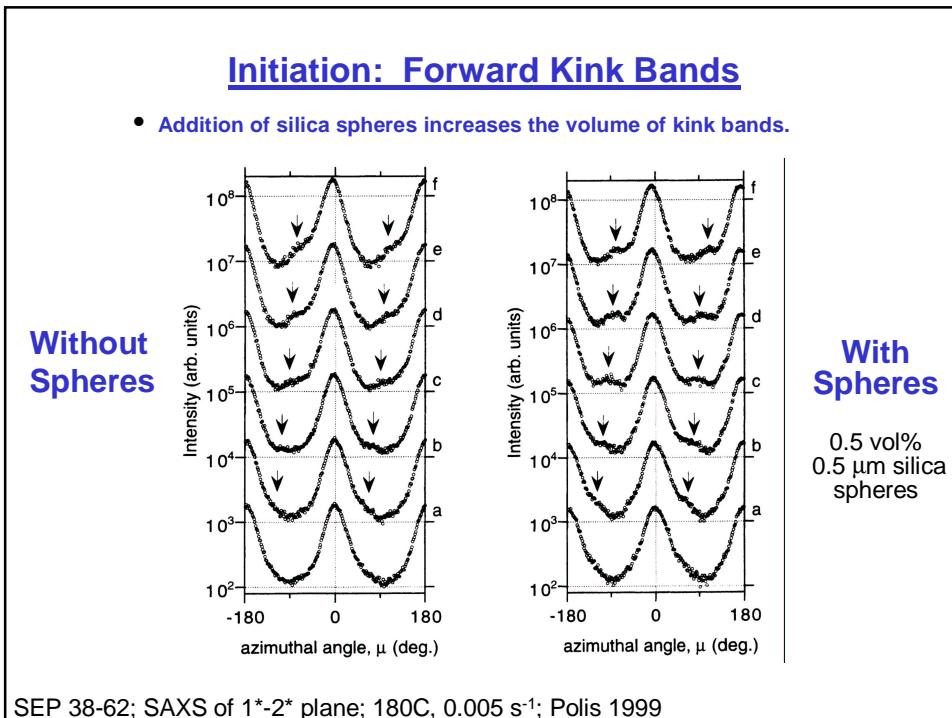
Starting State

(LAOS)

$$\gamma = 1$$

(180C, 0.001 s⁻¹)

SEP 40-70; TEM of 1-2 plane; shear to right; Qiao 2000



Initiation: Conjugate Kink Bands

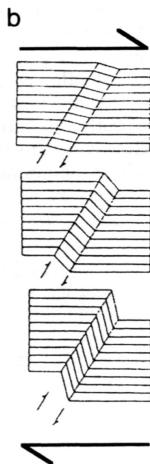
Figure 5, 4, 6

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

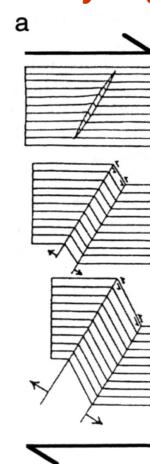
SEP 40-70; FE-SEM of 1-2 plane; Polis 1996

Dynamics: Forward Kink Bands

Lamellar rotation

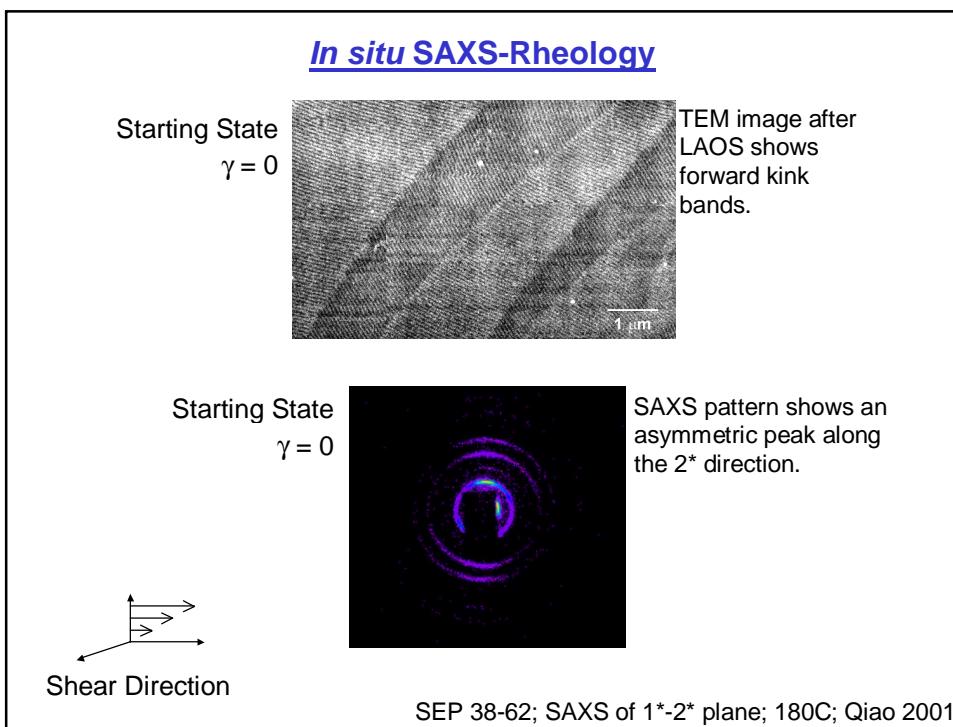
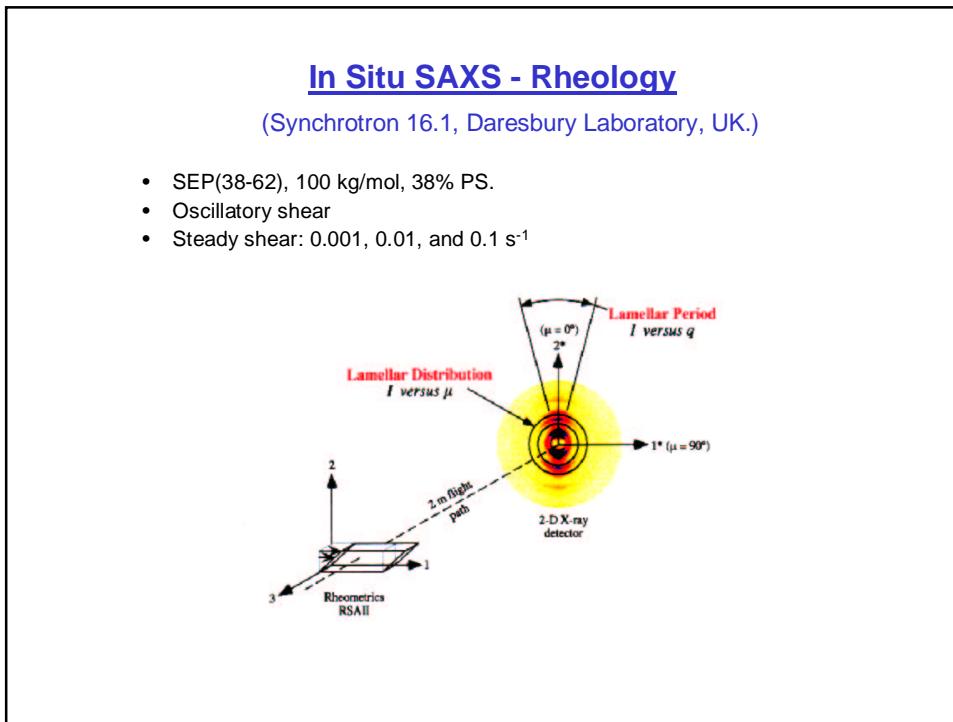


Boundary migration

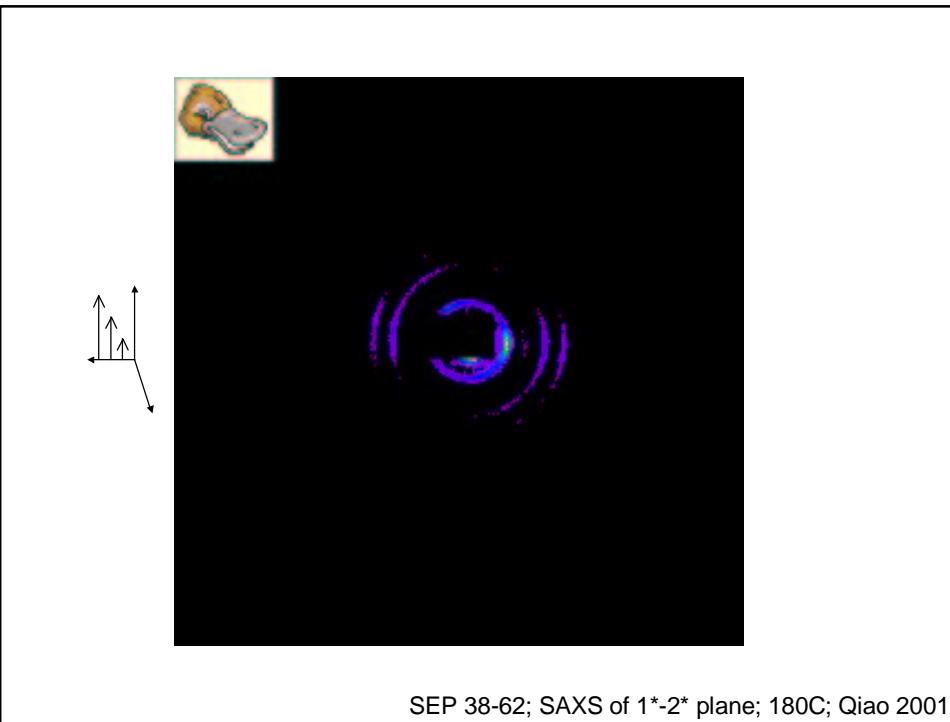
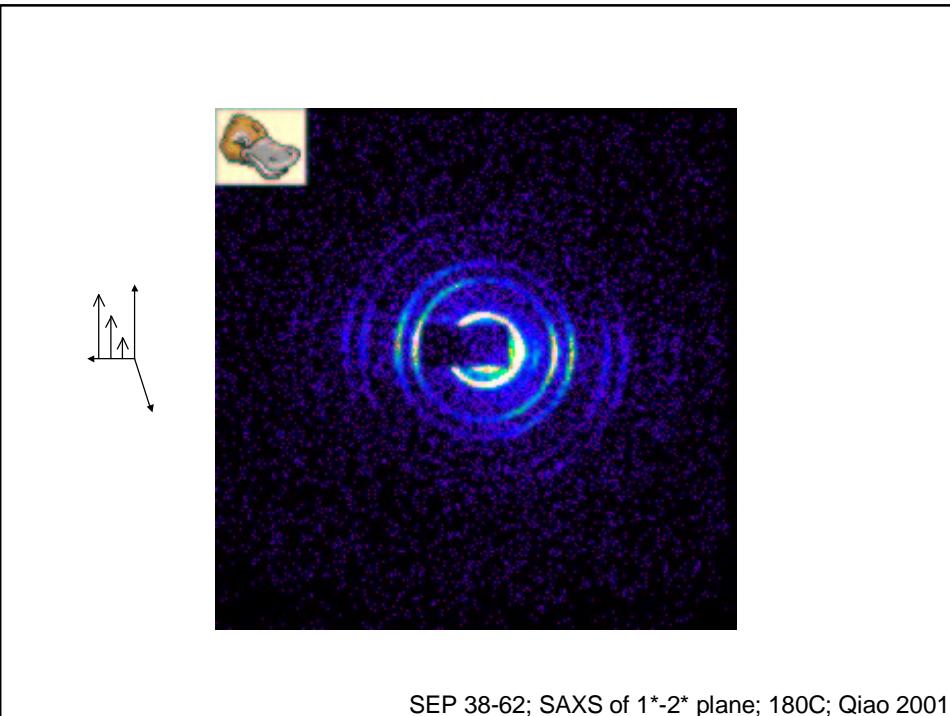


- Lamellae inside k.b. **rotate** w/ strain
- Constant k.b. width
- Lamellae orientation inside k.b. **fixed**
- Increasing k.b. width w/ strain

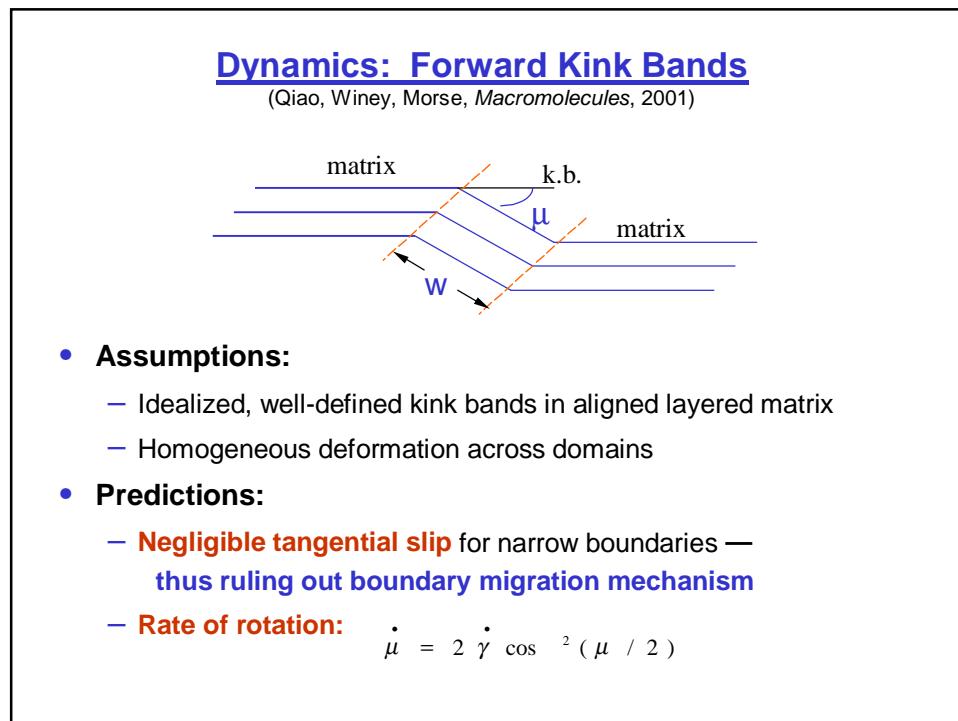
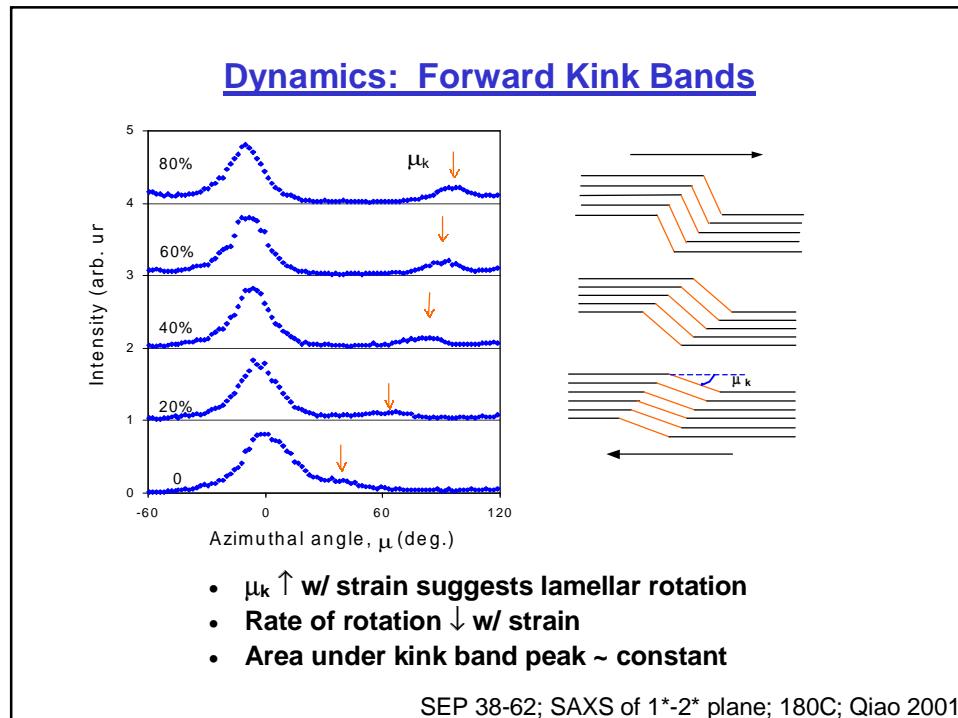
Kink Bands in Block Copolymer Lamellar Phases



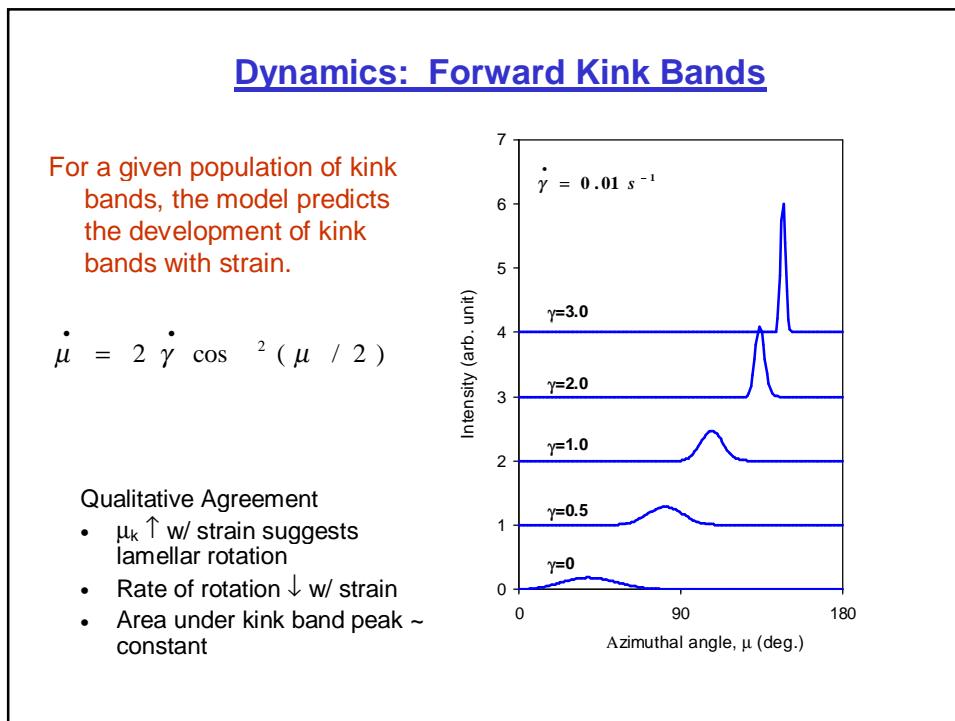
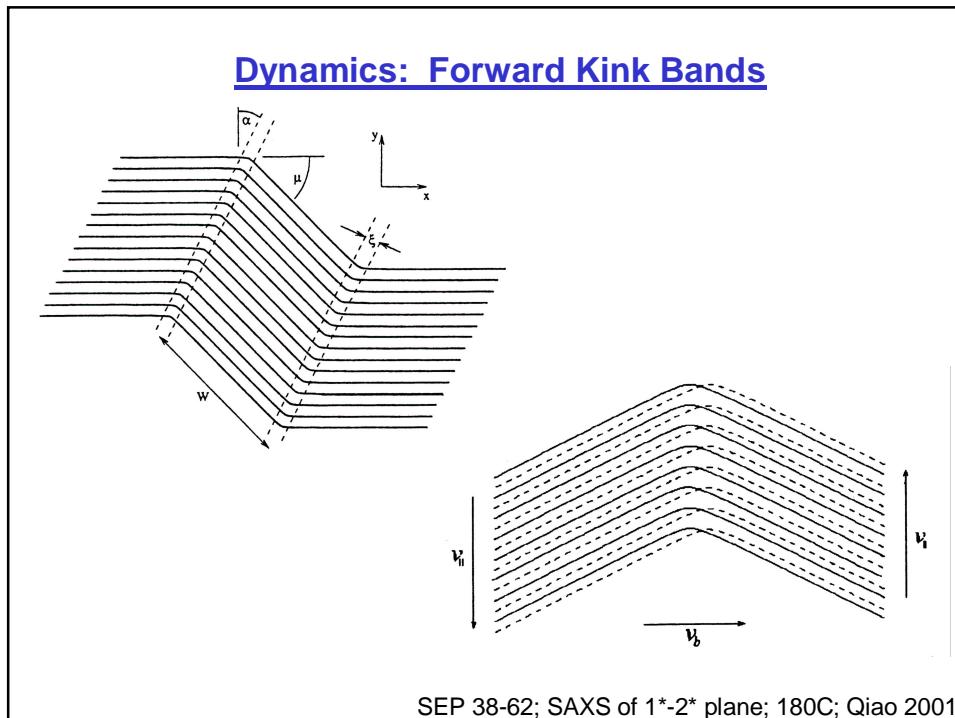
Kink Bands in Block Copolymer Lamellar Phases



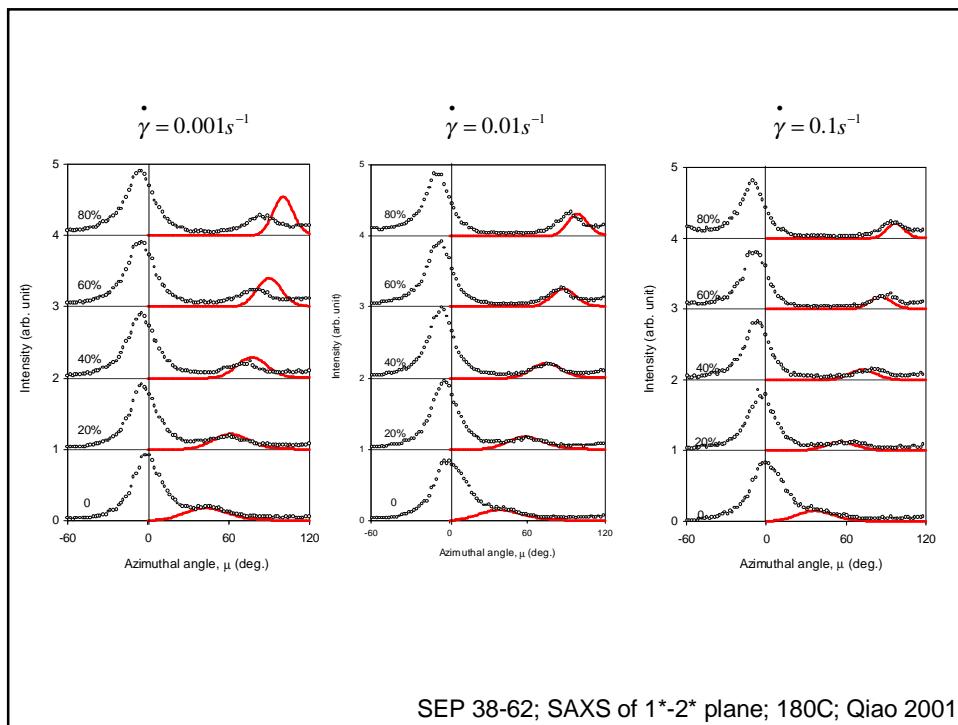
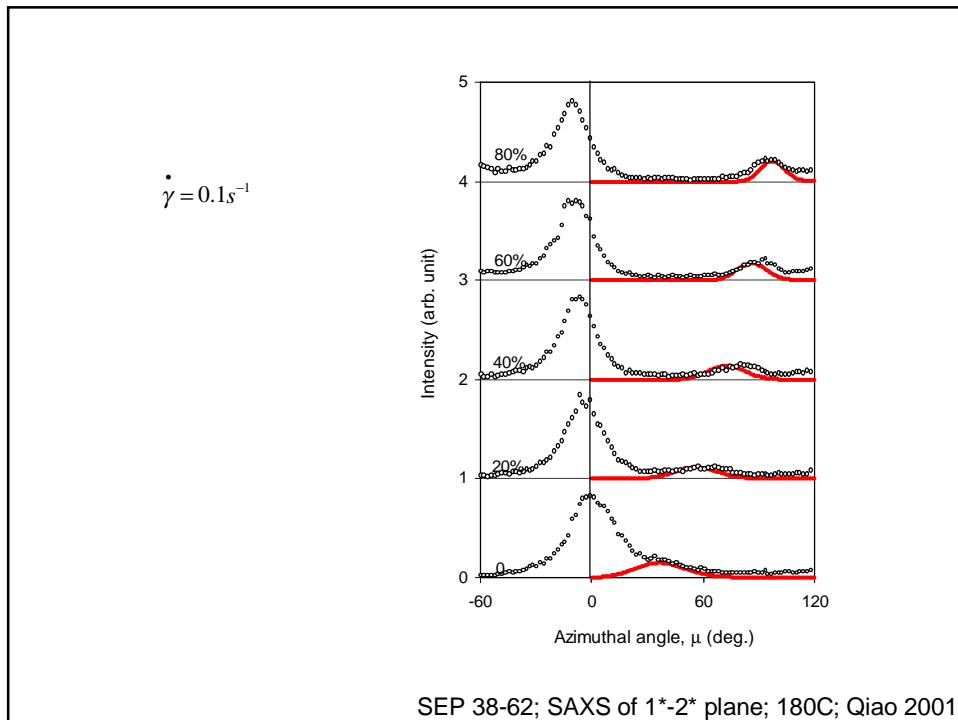
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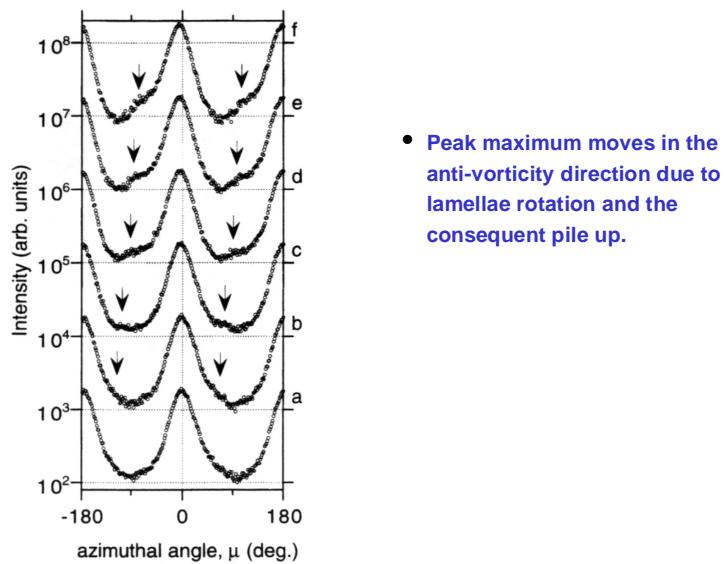
How do kink bands evolve w/ strain?

- Kink bands evolve through **lamellar rotation**, the **rate of rotation** follows:

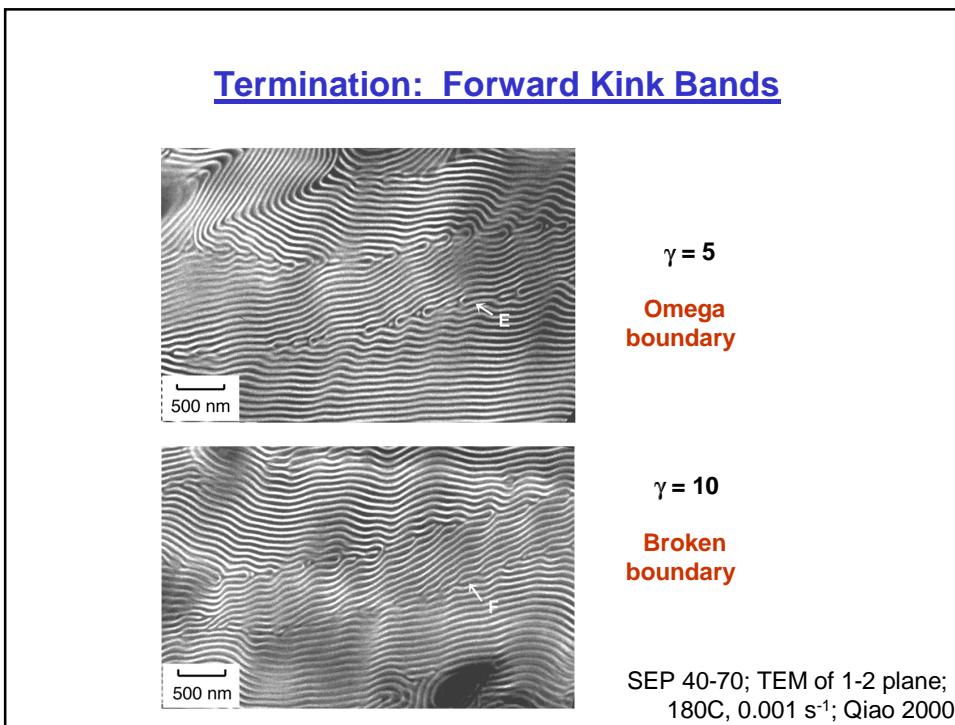
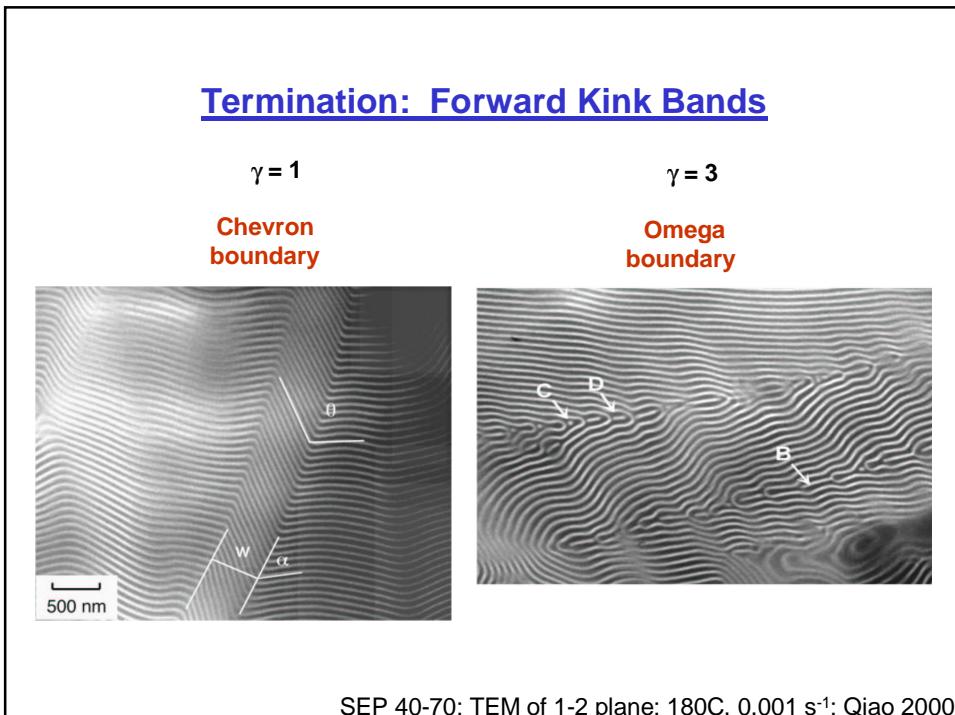
$$\dot{\mu} = 2 \dot{\gamma} \cos^2(\mu/2)$$

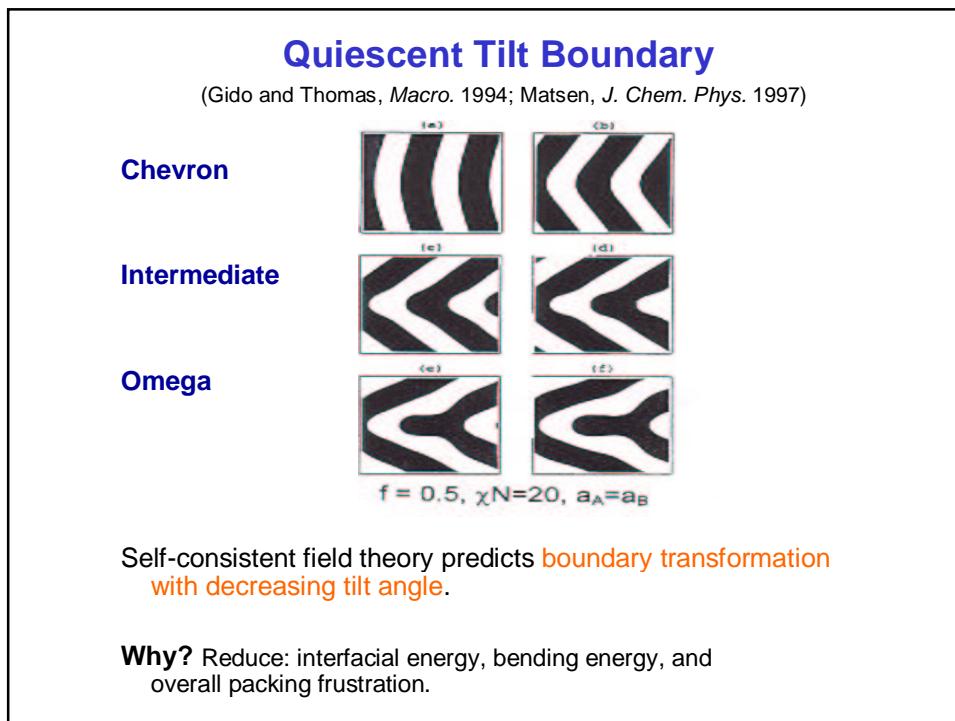
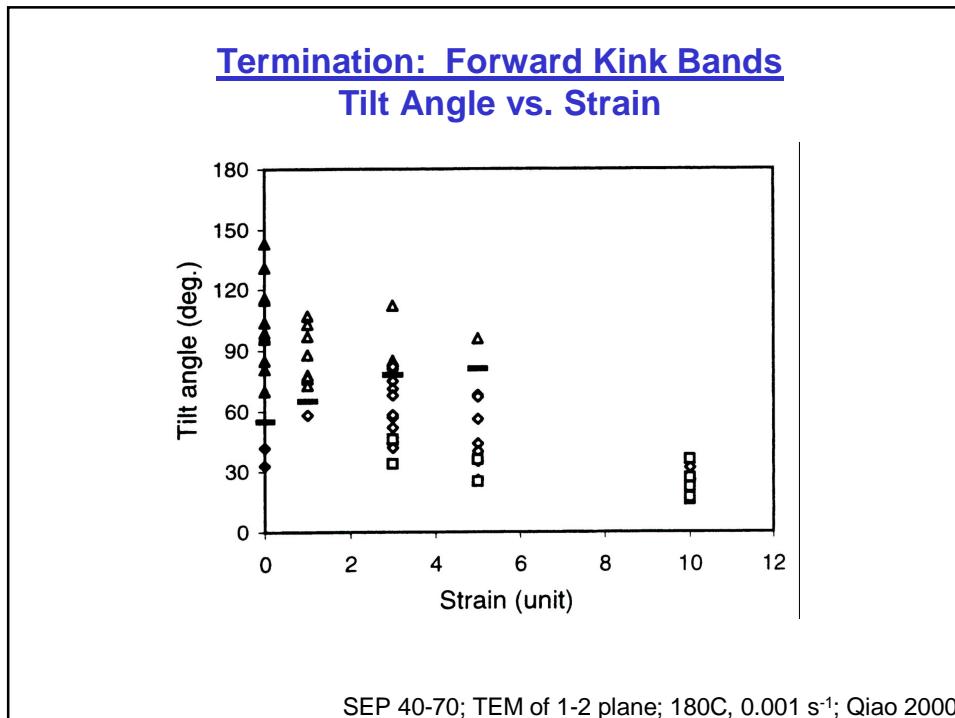
- The predicted rate of rotation shows an **accurate fit at the highest shear rate**.
- Deviations at lower rates are presumably due to the presence of spontaneous *domain relaxation*.

Dynamics: Forward Kink Bands



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





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

Qiao and Winey, *Macromolecules* 33(3), 851-856 [2000].

- 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, 150C, g=40%, 1 s⁻¹
- Anneal: 150C, 2h

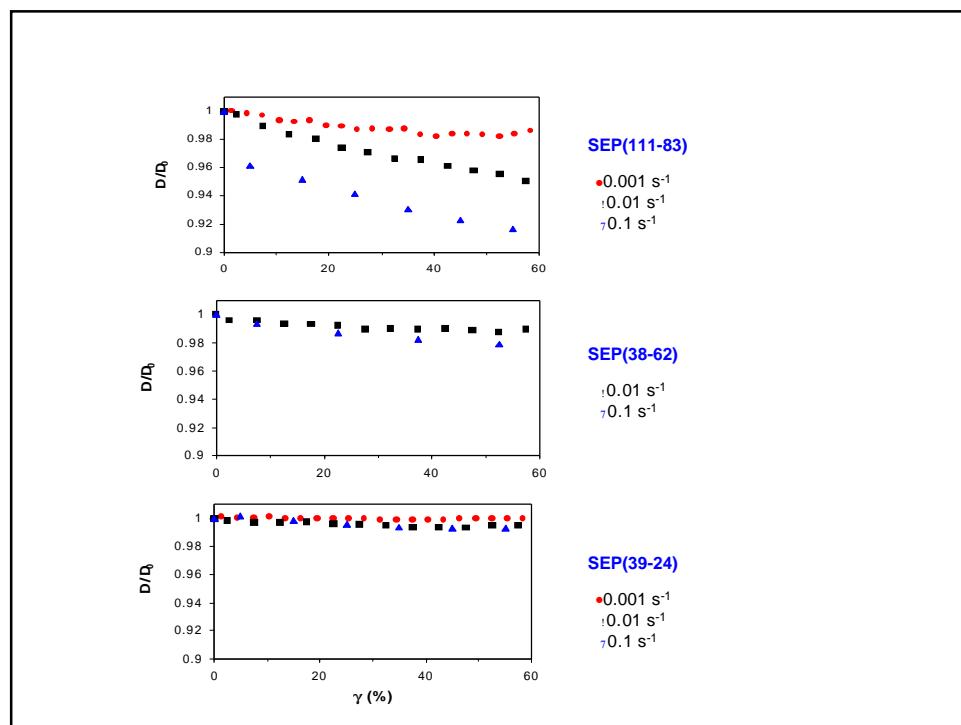
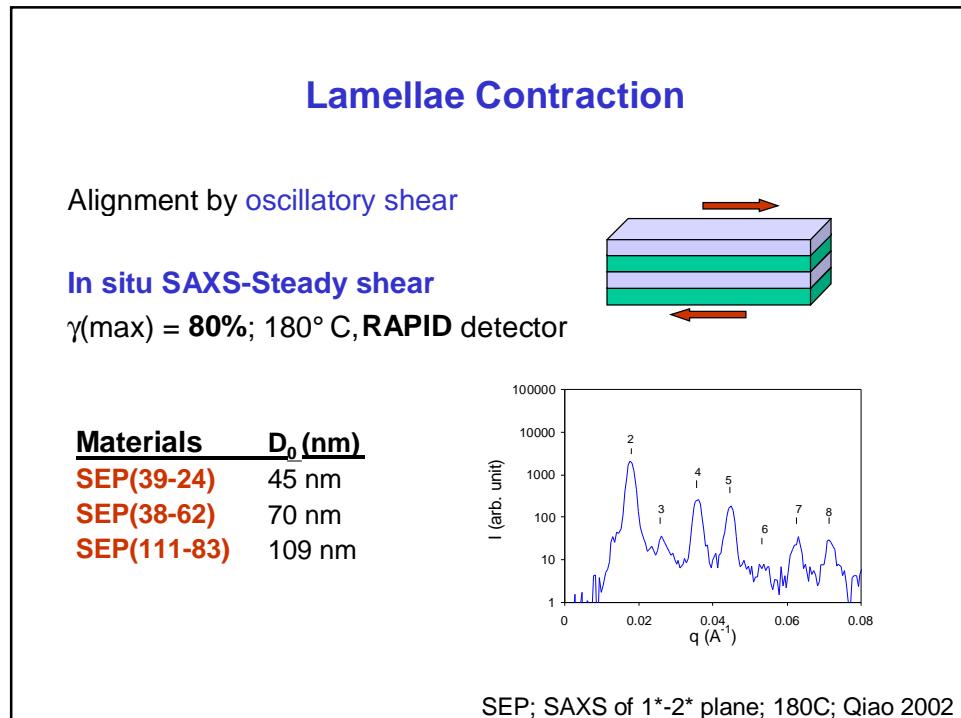
SEP 40-70; FE-SEM of 1-2 plane; Polis 1996

Relaxation: Conjugated Kink Bands

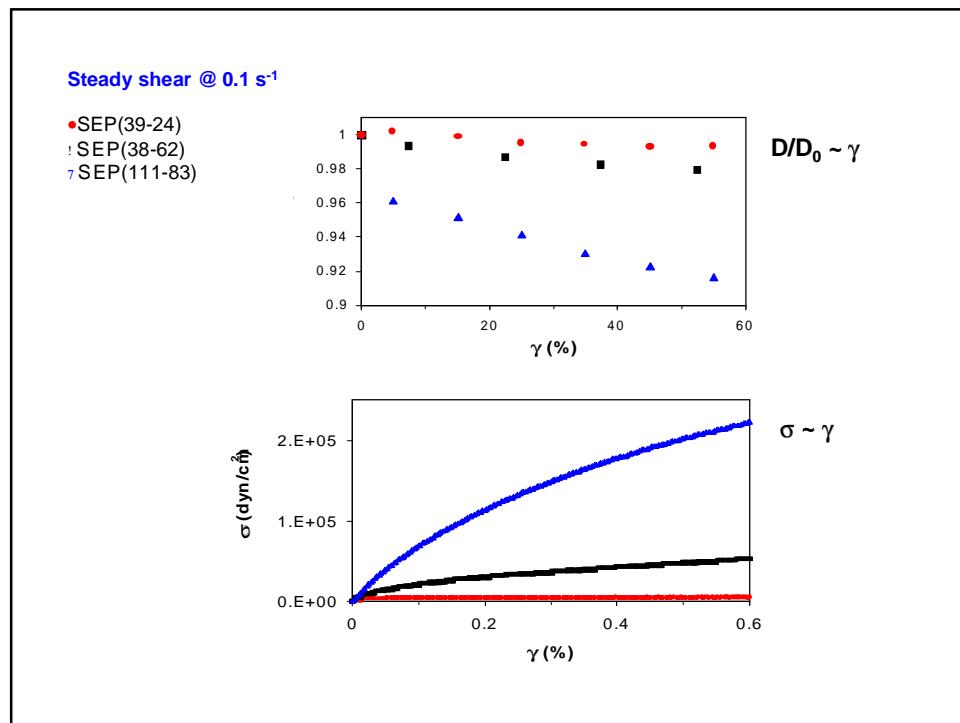
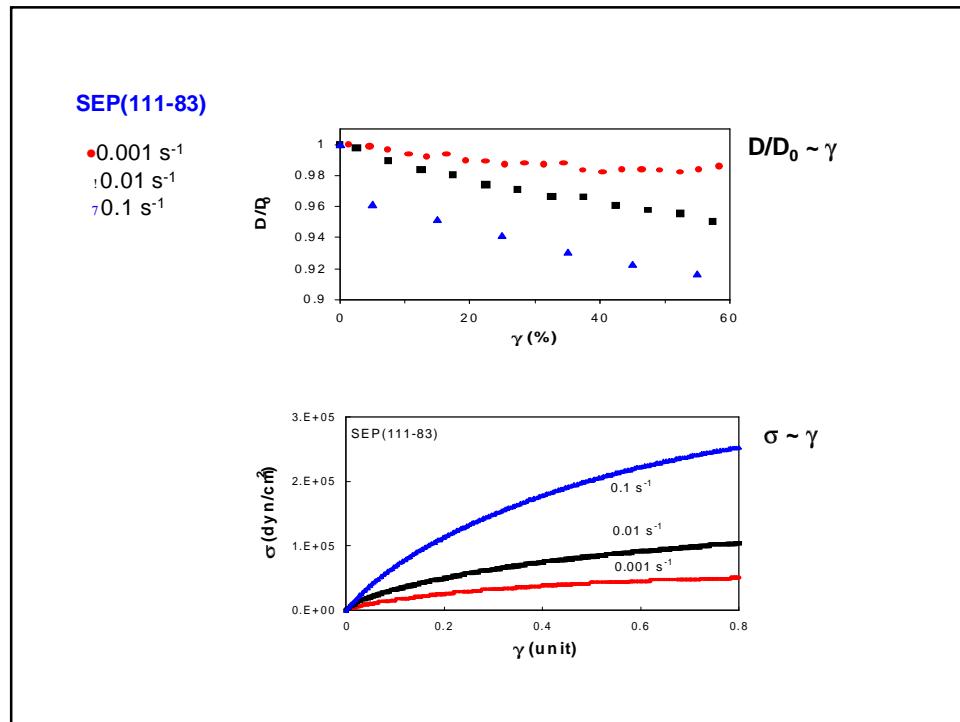
- As molded starting state
- Large Amplitude Oscillatory Shear: 12h, 150C, g=40%, 1 s⁻¹
- Anneal: 150C, 48h

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

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



Kink Bands in Block Copolymer Lamellar Phases



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

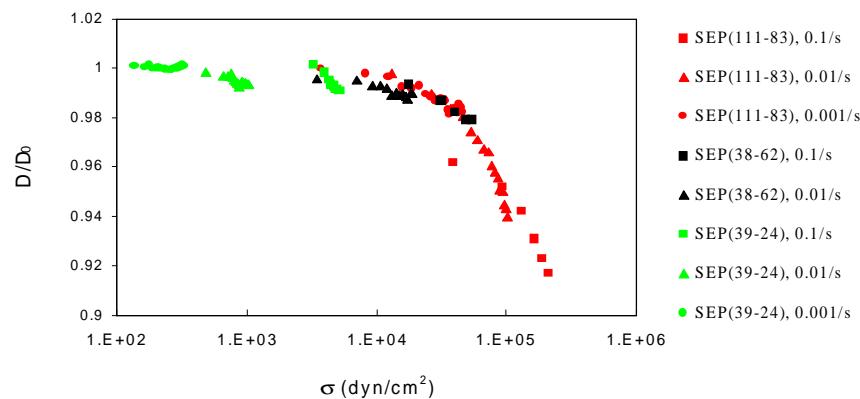
Constraints on Morphology:

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:

(Williams & MacKintosh, *Macromolecules* 1994)

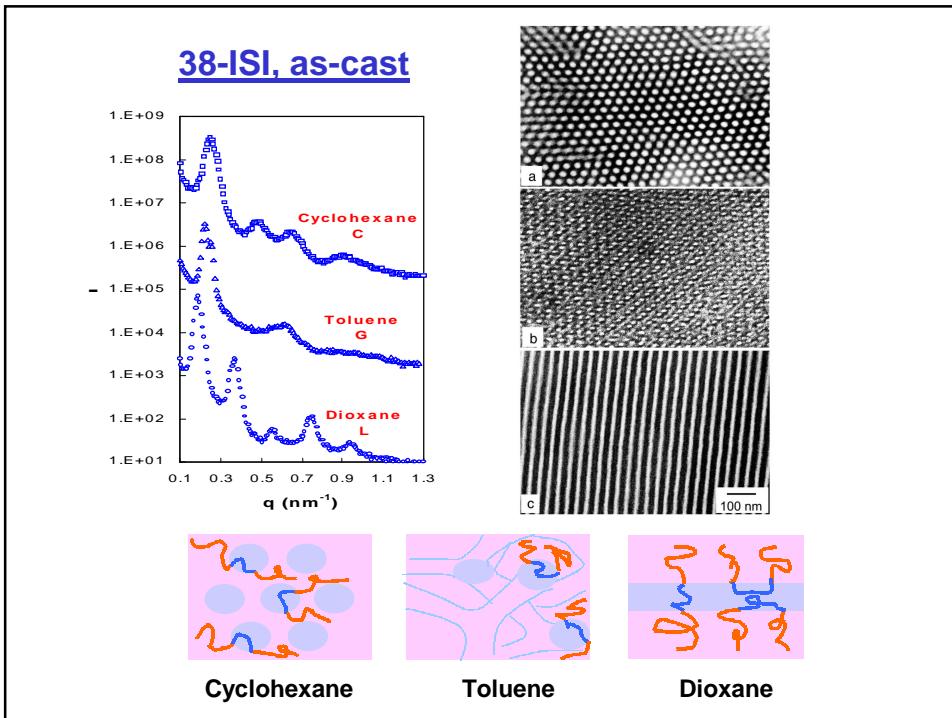
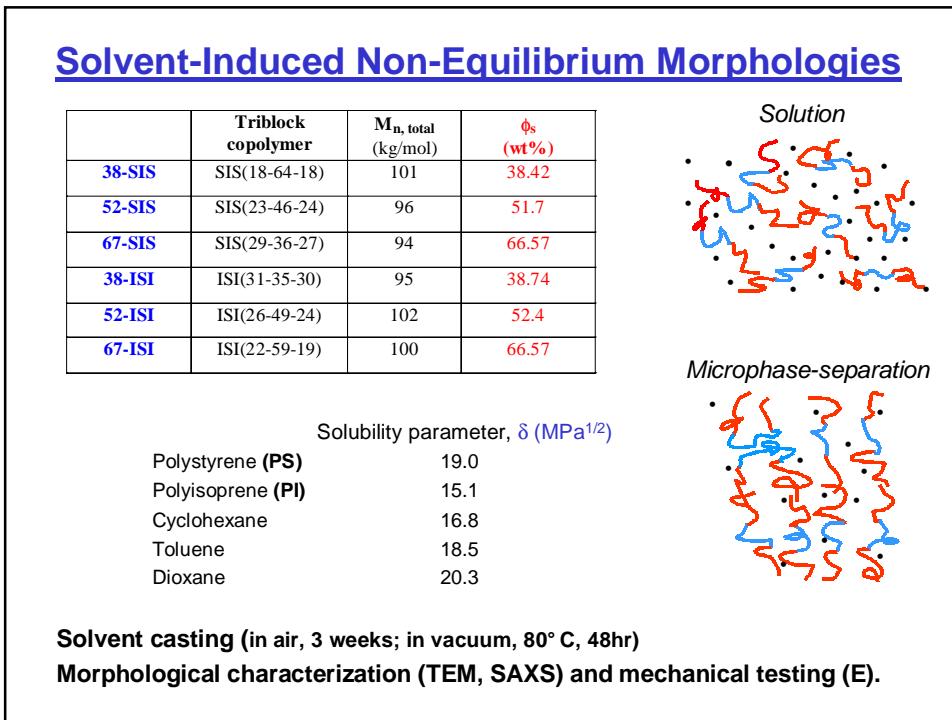
Assumption:

Elastic distortion

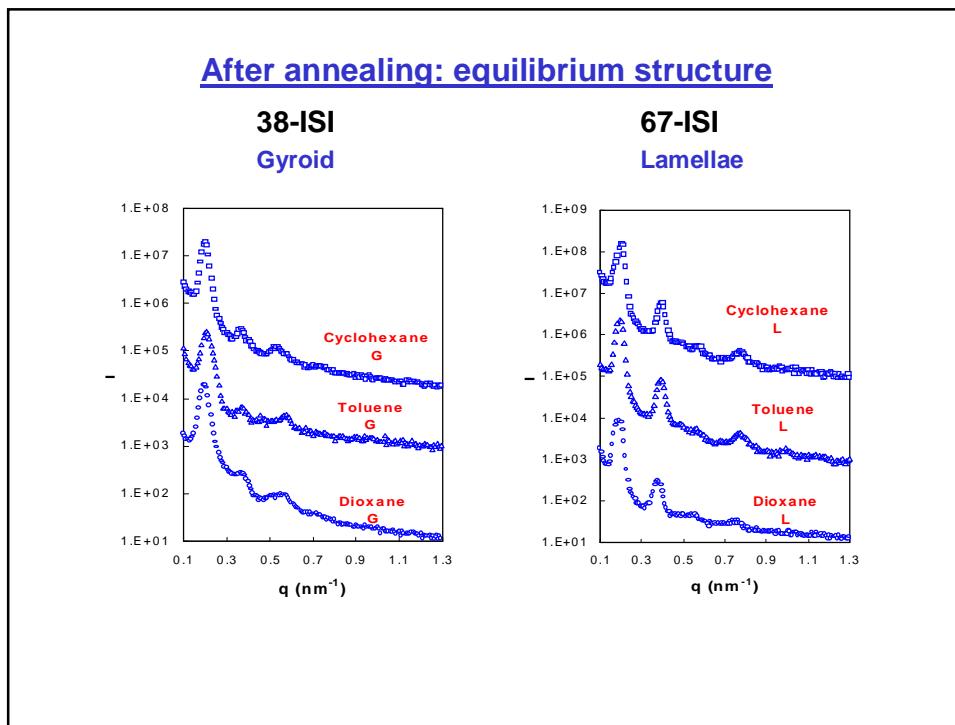
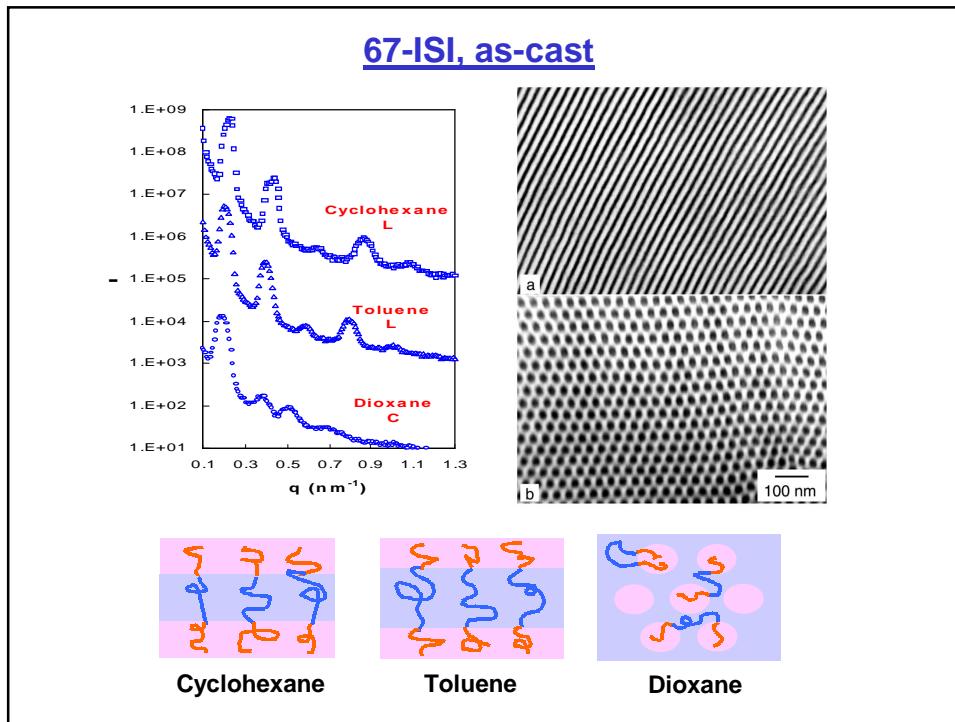
Constant stress, uniform strain across lamellae

Prediction: $(D-D_0)/D_0 \sim -\sigma^2/(\sigma^2+3G^2)$

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Kink Bands in Block Copolymer Lamellar Phases

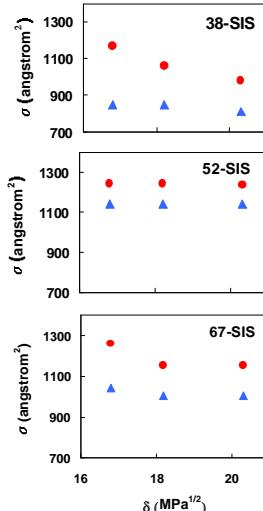
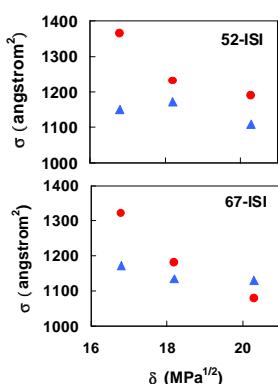
As-cast → Annealed

ISI		As cast → Annealed		
Solvent	Solubility parameter, δ (MPa $^{1/2}$)	38-ISI	52-ISI	67-ISI
Cyclohexane	16.8	C → G	L+G → L	L → L
Toluene	18.5	G → G	L → L	L → L
Dioxane	20.3	L → G	L → L	C → L

SIS		As cast → Annealed		
Solvent	Solubility parameter, δ (MPa $^{1/2}$)	38-SIS	52-SIS	67-SIS
Cyclohexane	16.8	C → L	L → L	L → C
Toluene	18.5	L → L	L → L	C → C
Dioxane	20.3	L → L	L → L	C → C

Area per Junction

- As-cast
- ▲ Annealed



• Area per junction larger in as-cast samples.

• Effect of solvent is influenced by the solubility parameter and evaporation rate.

Modulus vs. As-Cast Morphology, chain architecture

ϕ_s (%)	Solvent	Morphology	SIS (ksi)	ISI (ksi)
3.8	Cyclohexane	C	10.1	5.4
3.8	Toluene	G	—	14.0
3.8	Toluene	L	19.8	—
3.8	Dioxane	L	21.0	7.8
5.2	Toluene	L	23.2	17.8
5.2	Dioxane	L	32.6	22.2
6.7	Toluene	C	102.9	—
6.7	Toluene	L	—	34.3
6.7	Dioxane	C	73.2	42.3

- E ↑ w/ ϕ_s : 38-SIS < 52-SIS < 67-SIS.
- E ↑ w/ **domain connectivity**:
 - PS cylinders < Lamellae < Double Gyroid.
 - Lamellae < PI cylinders.
- E ↑ w/ **trapped entanglements**: SIS > ISI.