Necking Instability in Polydomain Main-Chain Smectic Elastomers

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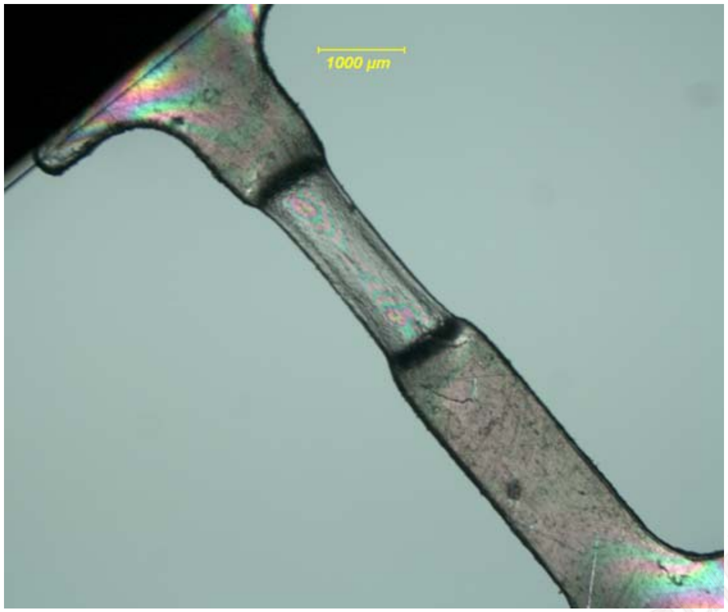
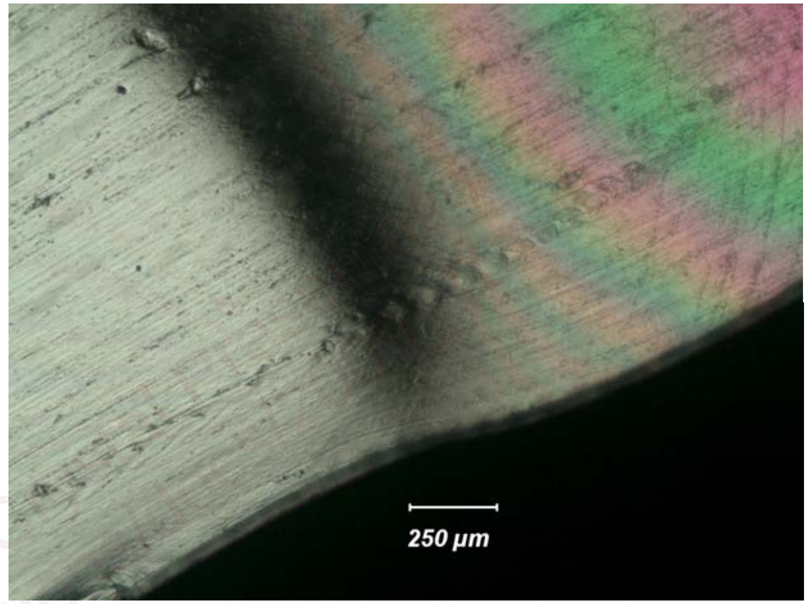
Necking Instability



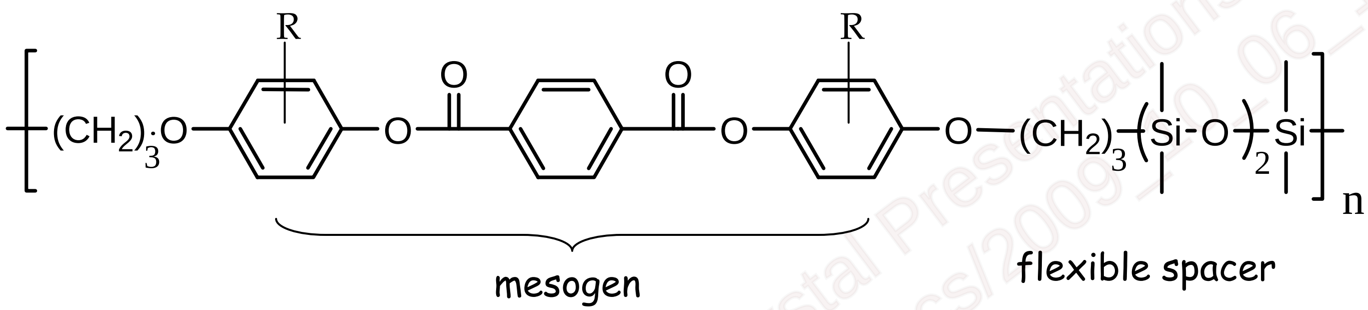


Necking is a macroscopically inhomogeneous deformation that has been well-studied in linear polymers for decades, but it has less frequently been observed in elastomers.

Inhomogeneous deformations in LCE are important due to widespread use of uniaxial elongation to prepare monodomain LCE, and due to fundamental interest in the mechanical response of LCE subjected to elongation.

Our Materials: Non-Crosslinked LC Polymers

backbone repeat unit



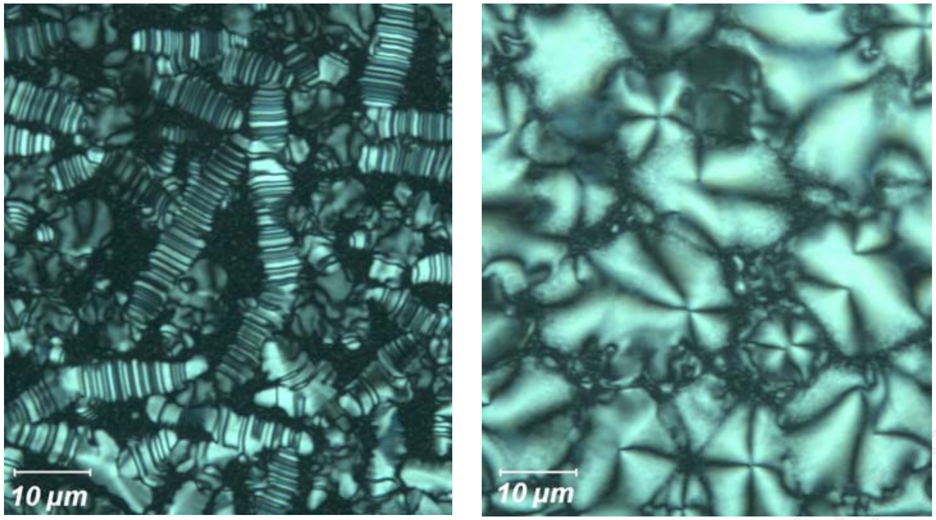
central terephthalate group

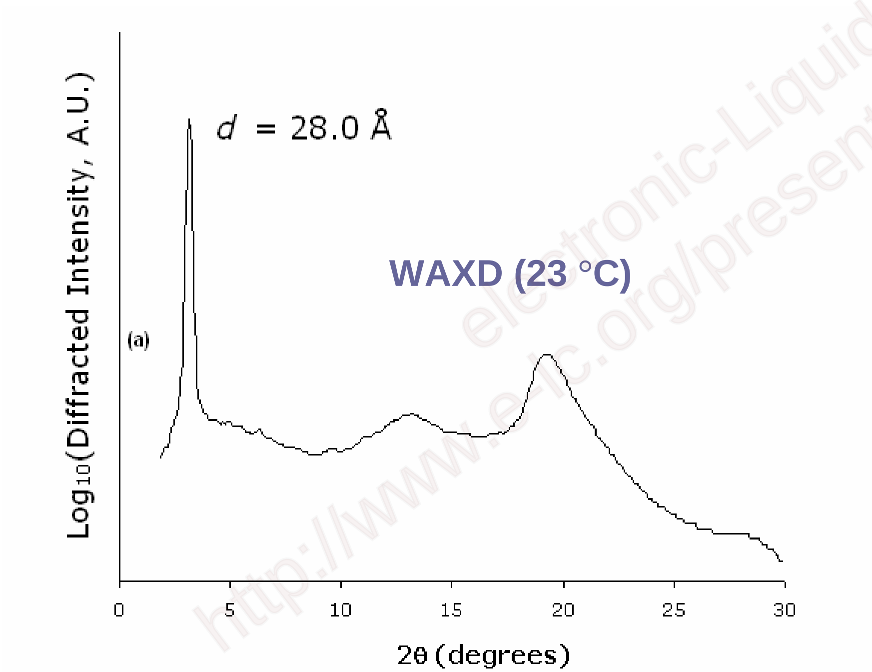
R = H, CH_3, Cl, OCH_3, $COCH_3$, or tBu

Todays' talk: R = H throughout

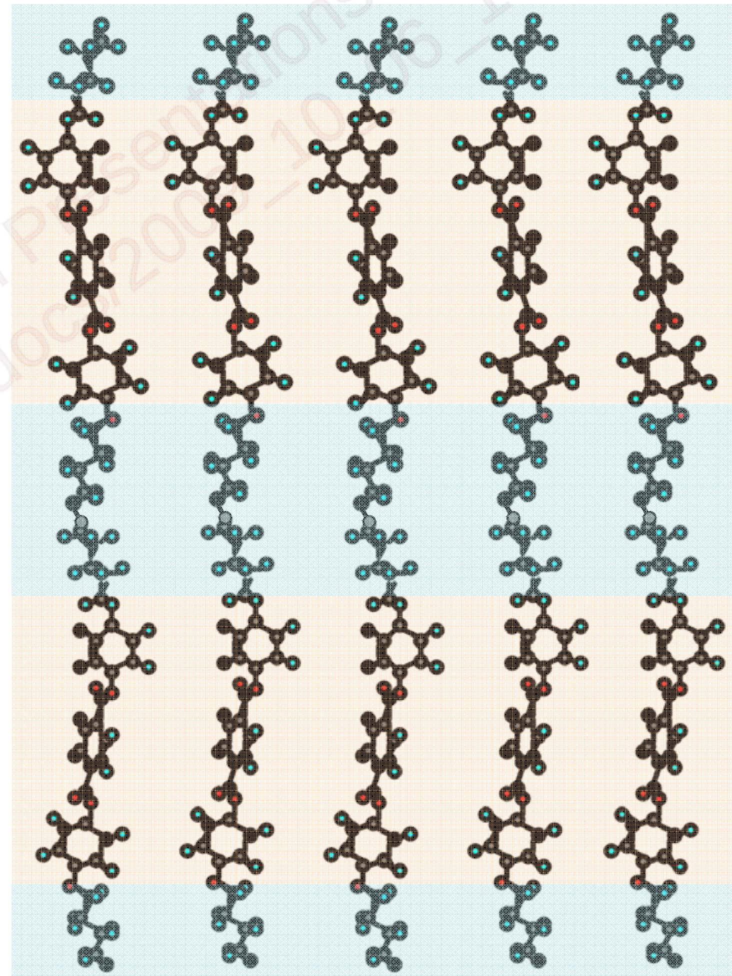
LC Phase Identification (Non-Crosslinked Polymer)

Optical textures





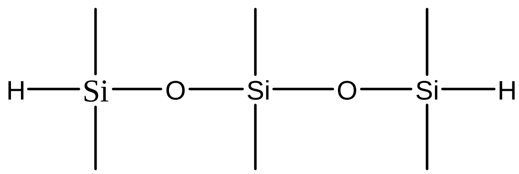
Smectic C_A phase



"Zig-zag" mesogen tilt angle

Our Materials- Elastomers

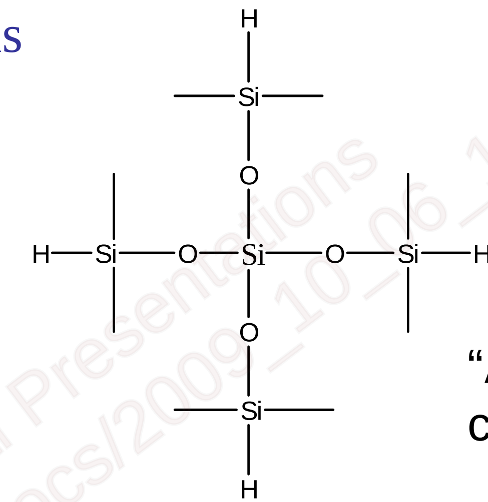
One-Pot Synthesis



1,1,3,3,5,5 hexamethyltrisiloxane

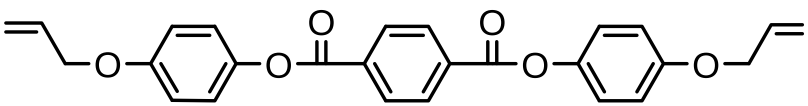
"**A_2**" flexible segment

Pt-catalyzed hydrosilylation

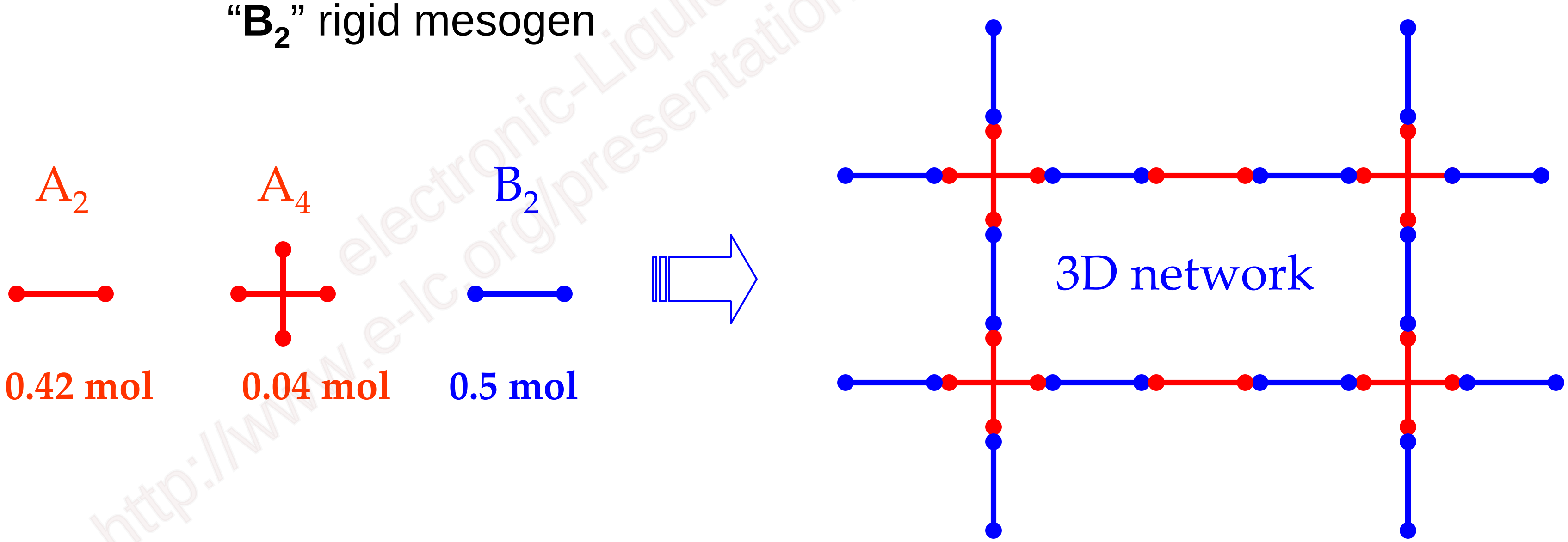


tetra-*kis*-dimethylsiloxysilane

"**A_4**" flexible crosslinker



"**B_2**" rigid mesogen

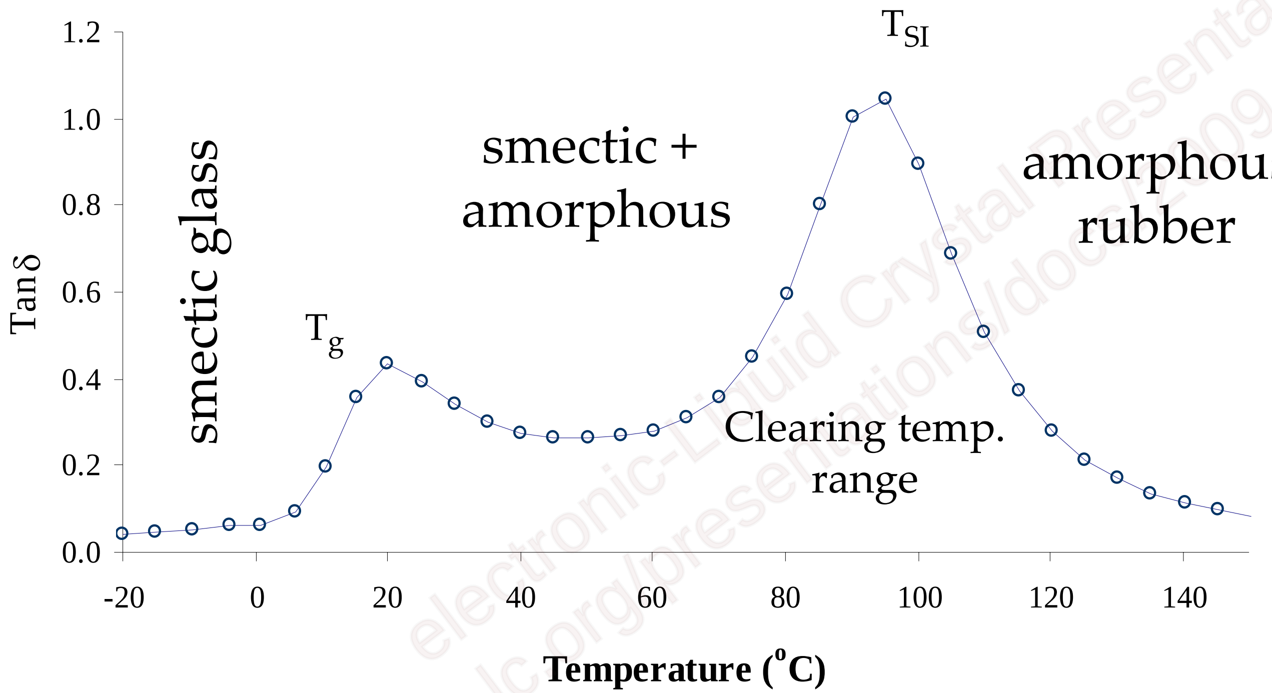


Crosslinking Conditions

- Crosslinking in solution (toluene) at 80 °C
- Close to bulk clearing temperature; isotropic state due to solvent
- No external aligning field → polydomain morphology

MCLCE Thermomechanical Behavior (Low Strains)

Small-strain ($\gamma_0 = 0.005$) oscillatory shear at ω=1 Hz

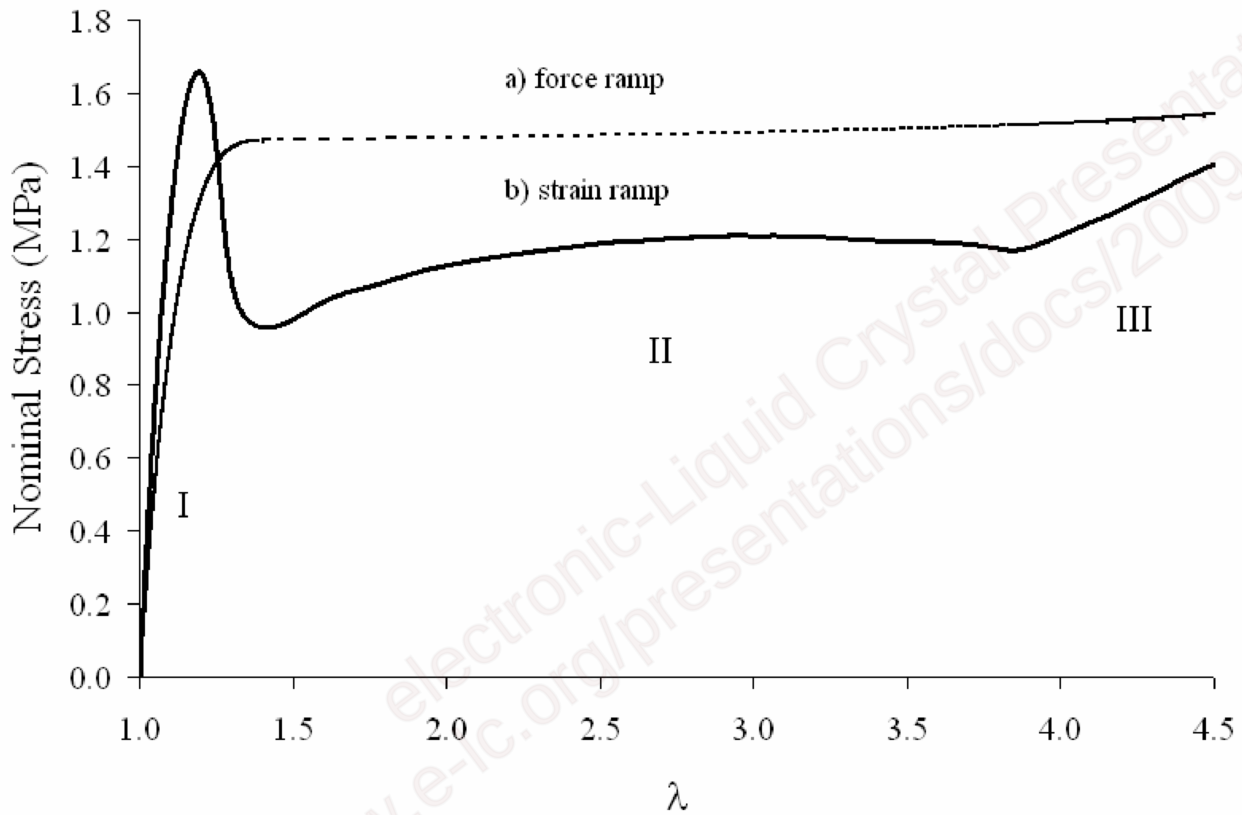


TA Instruments Q800 DMA

H. P. Patil, J. Liao, and R. C. Hedden, "Smectic Ordering in Main-Chain Siloxane Polymers and Elastomers Containing *p*-Phenyleneterephthalate Mesogens." *Macromolecules* **2007**, *40*, 6206-6216.

Main-Chain LCE: Force vs. Elongation

Uniaxial elongation at 35 °C, smectic state

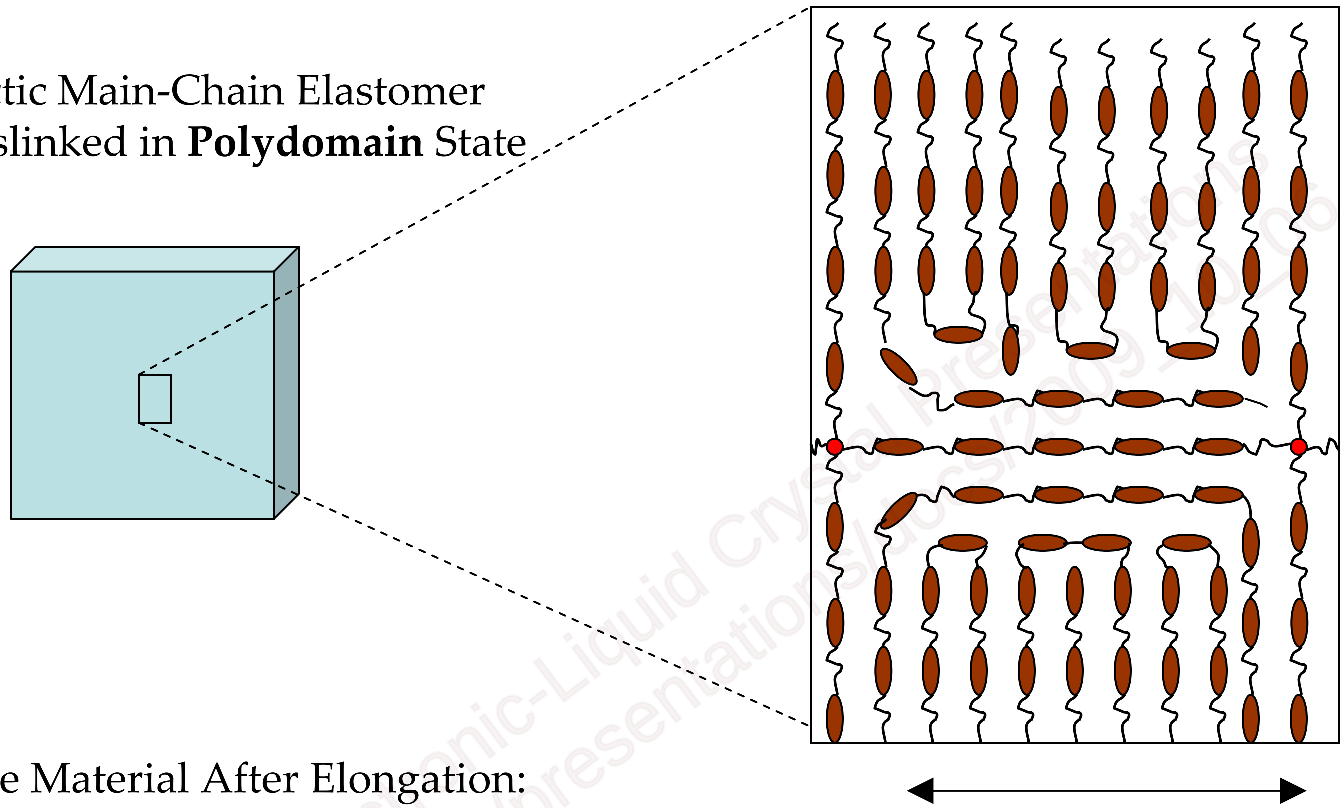


TA Instruments Q800 DMA

H.P. Patil and R.C. Hedden, "Necking Instability During Polydomain-Monodomain Transition in a Main-Chain Smectic Elastomer." Macromolecules 2009, 42, 3525-3531.

Polydomain-Monodomain (P-M) Transition

Smectic Main-Chain Elastomer
Crosslinked in **Polydomain** State

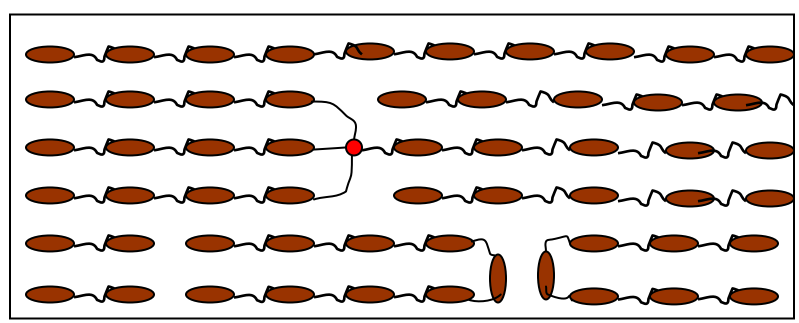


Numerous
Randomly
Oriented
Domains

Extensive
Chain
Folding
(Hairpins)

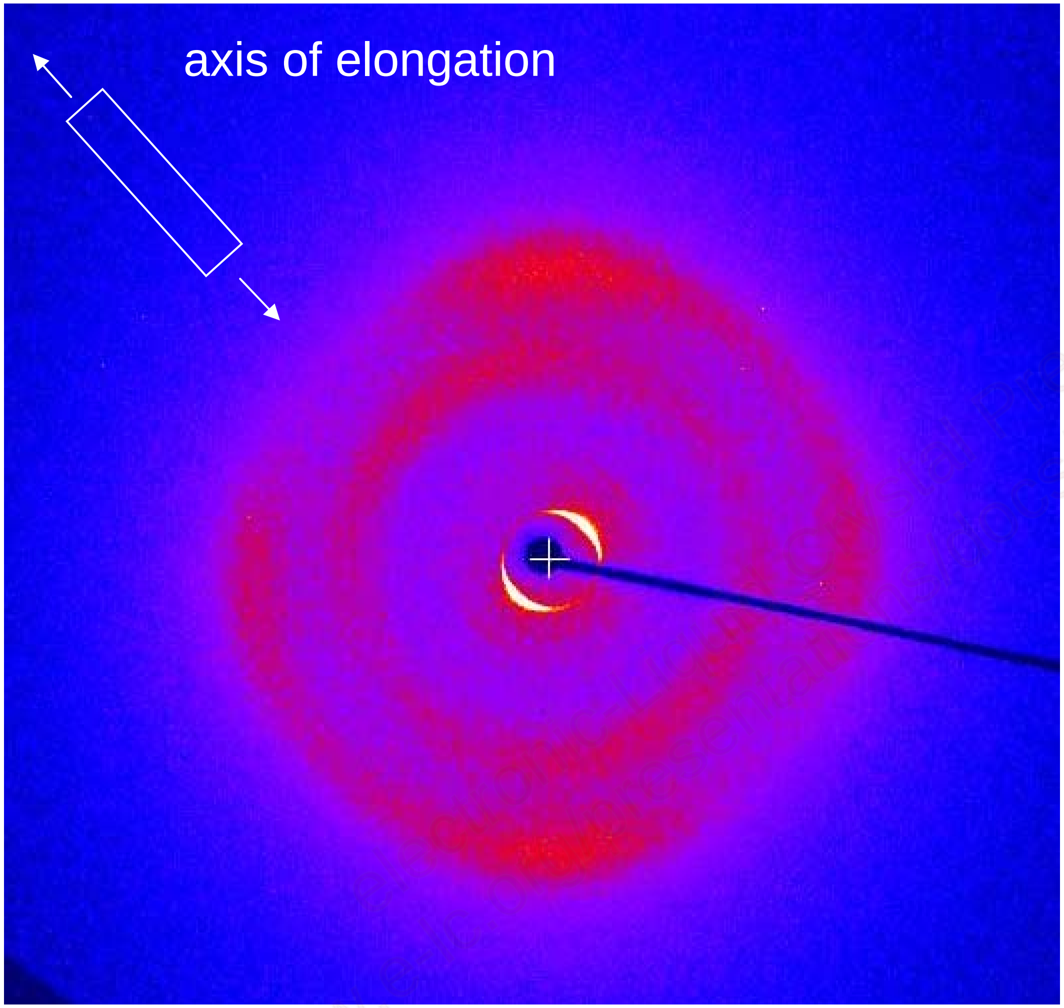
Same Material After Elongation:
Globally Oriented **Monodomain** State

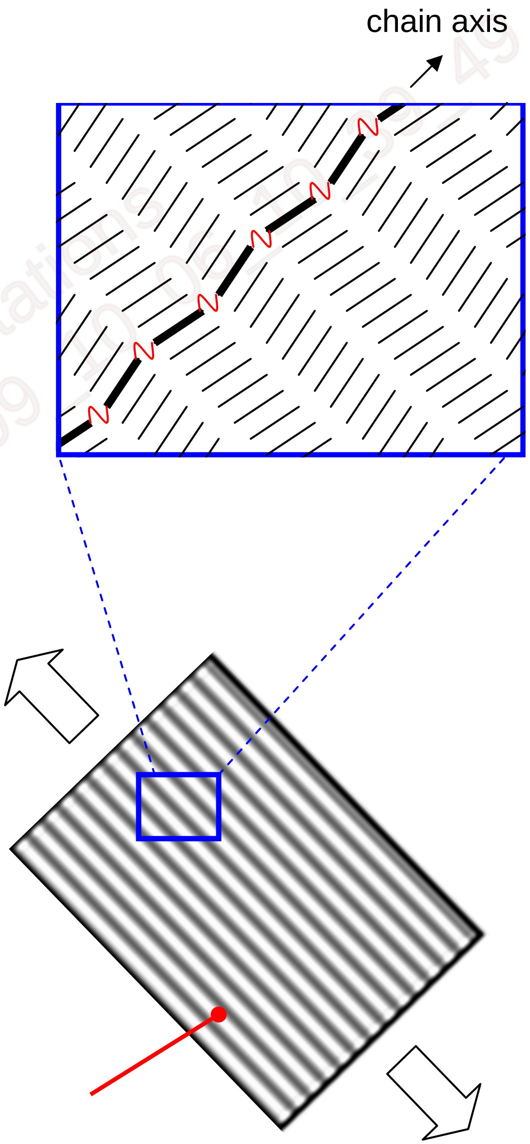
high strain $L/L_0 >> 2$



(some defects are still present)

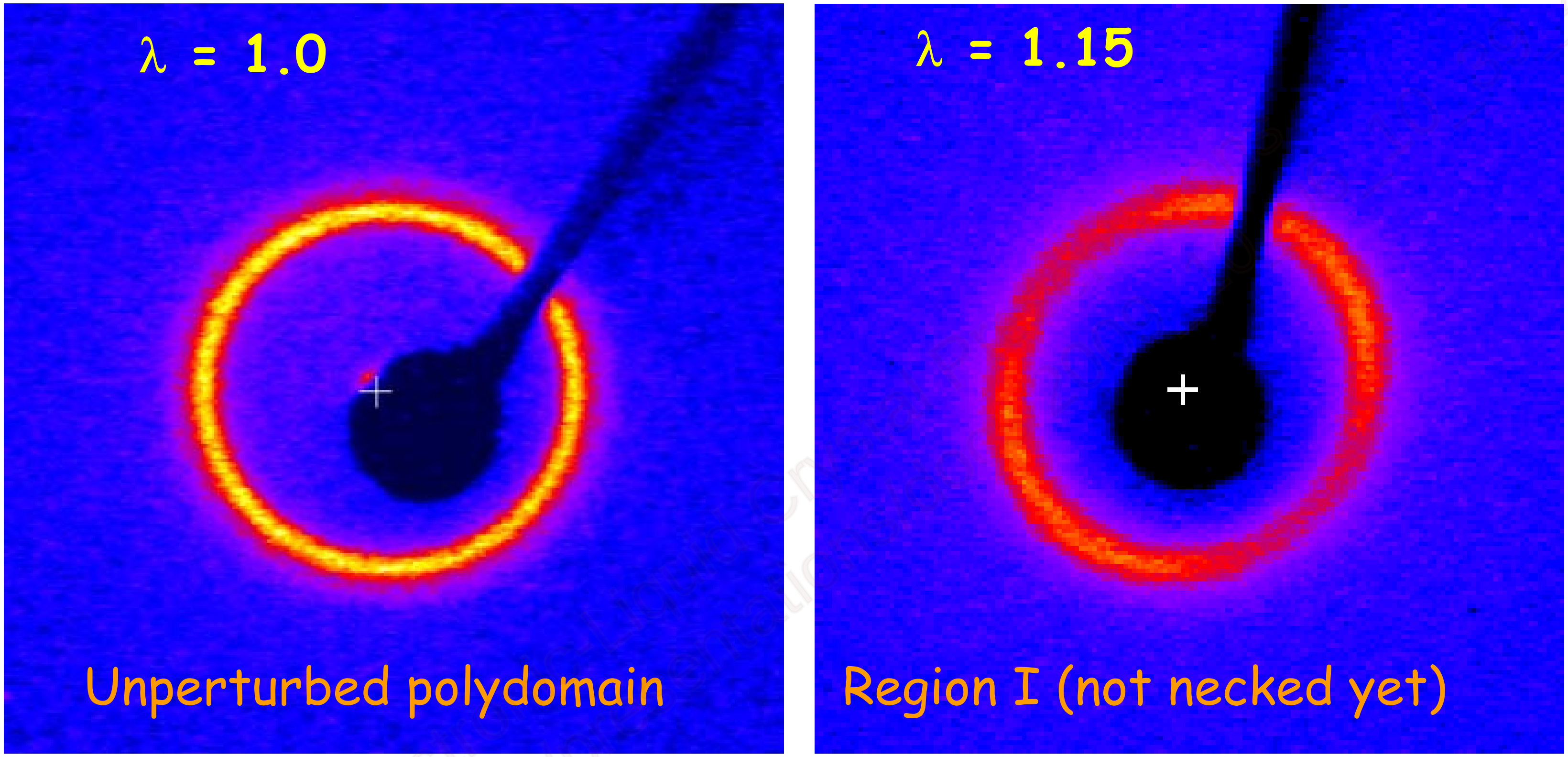
WAXD Evidence for Chain-Folding (Non-Crosslinked LCP)

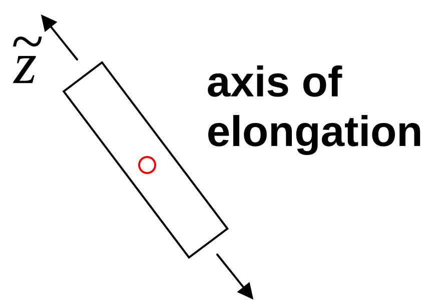




smectic layers *parallel* to elongation axis- "anomalous"

WAXD Evidence for Chain-Folding (Elastomer)



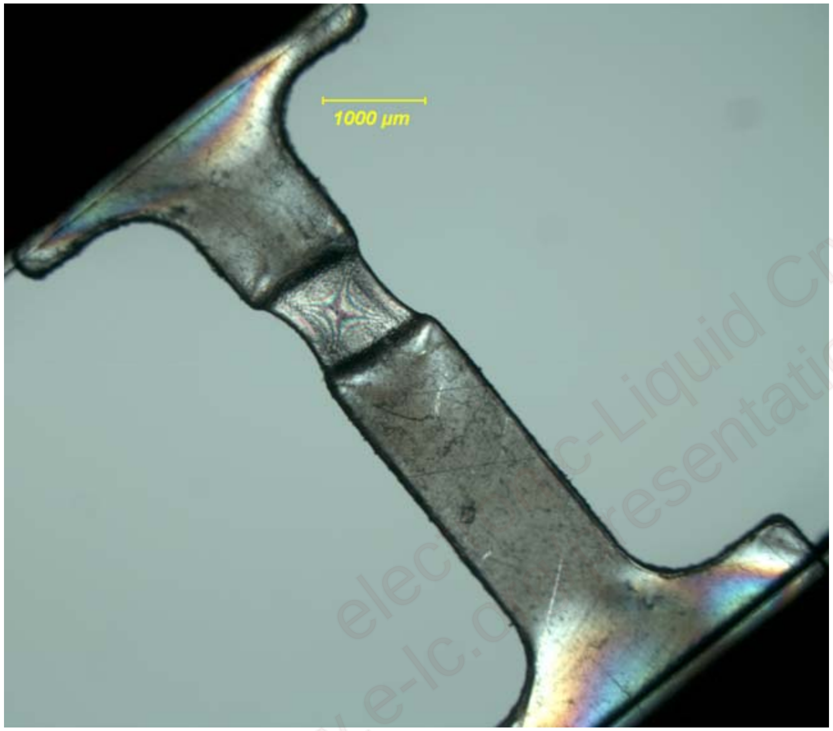


Anomalous (perpendicular) orientation of chain axes

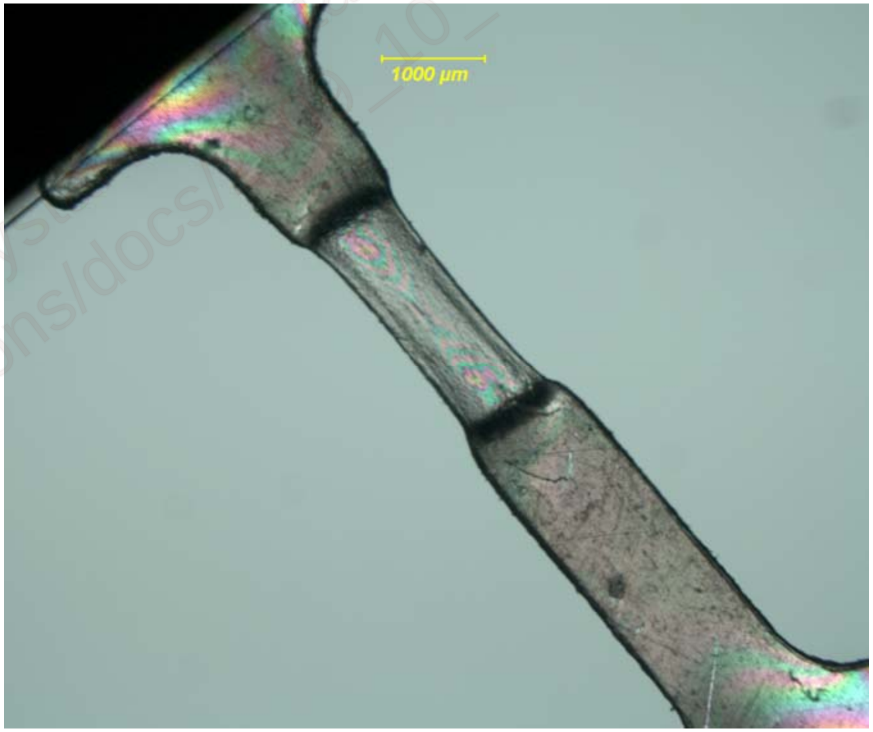
Necking Instability (Localized P-M Transition)

- Neck formation coincides with yielding (start of Region II, λ=1.17)

L/L_0 (overall) = 1.18

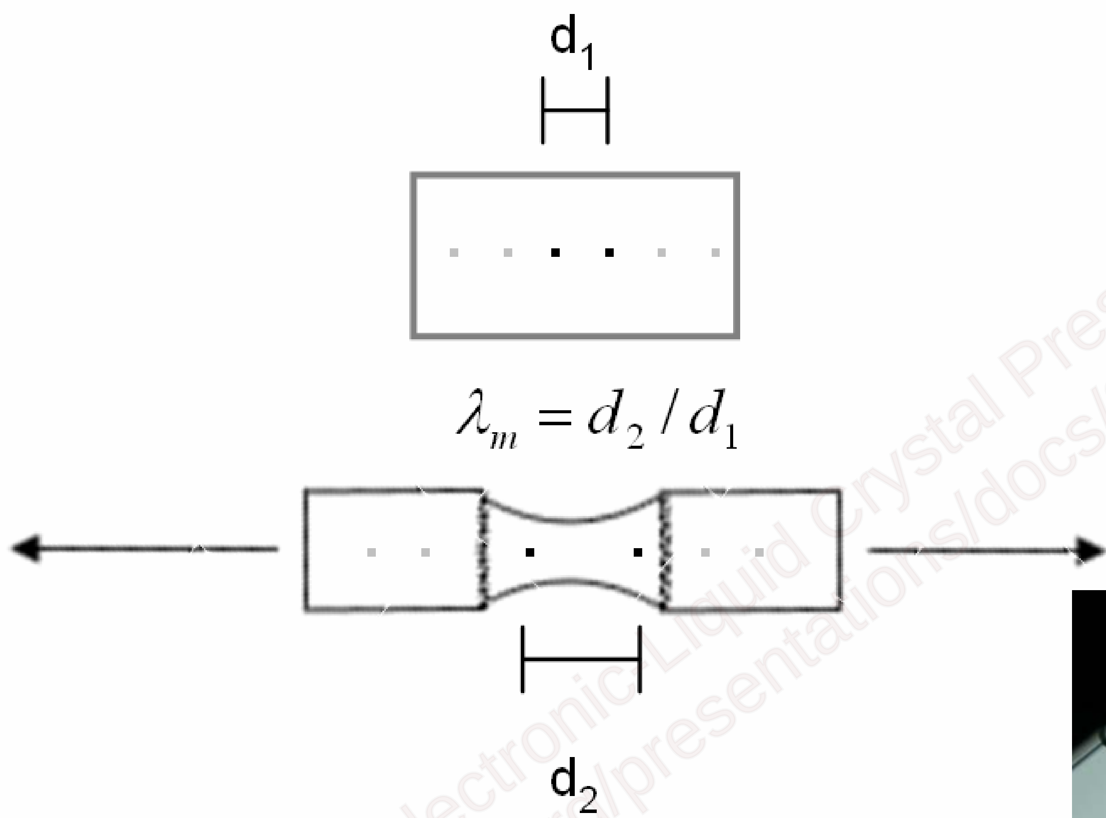


L/L_0 (overall) = 1.54

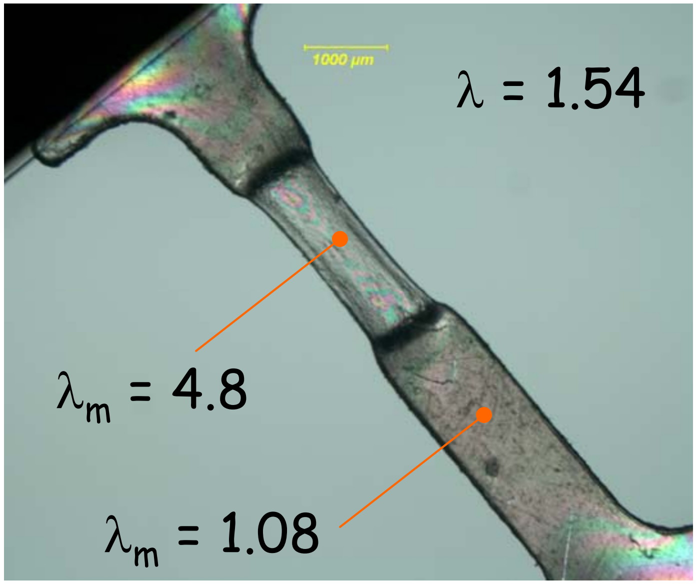


- "Neck" appears to consume polydomain material at its boundaries
- "Neck" reaches clamps at start of Region III

Measurement of λ_m via "Ink Dot" Technique

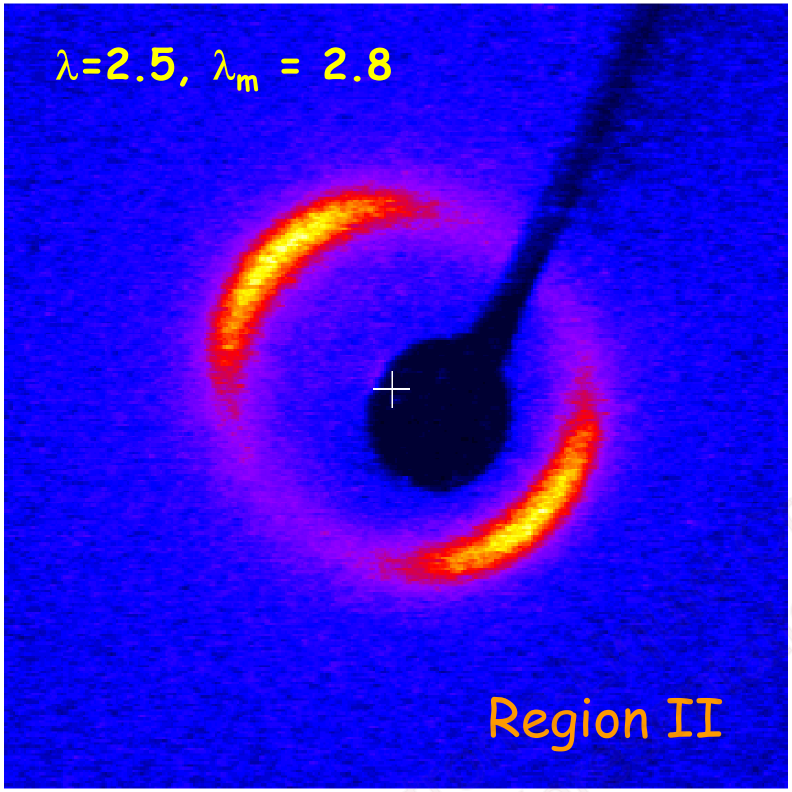


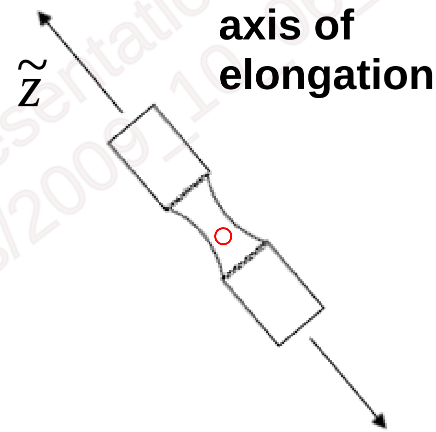
$$\lambda_m = d_2 / d_1$$



- Yielding begins at λ=1.17
- Polydomain material actually can relax somewhat after yielding

X-ray Diffraction: Region II





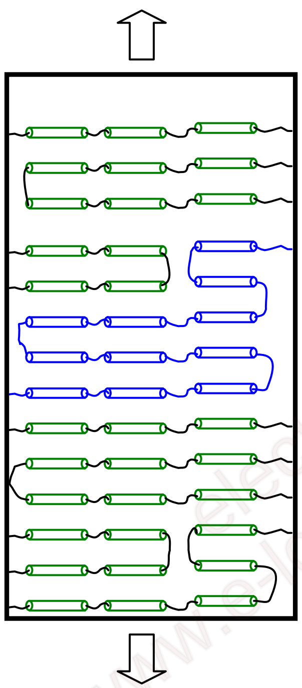
Normal (Parallel) orientation of chain axes

P-M Transition & Necking in Main-Chain LCE

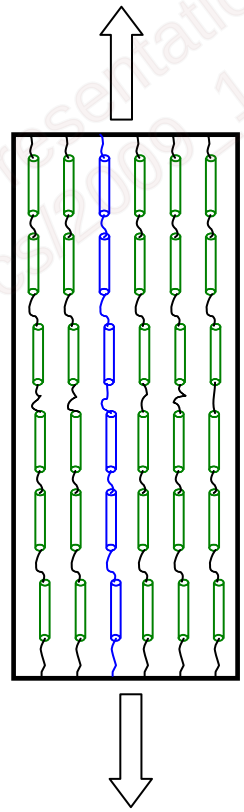
• Smectic microdomains are transiently destroyed as hairpins unfold.

• Necking is a local contraction resulting from loss of hairpins, which initiates at stress concentrators.

• New extended-chain smectic domains form.

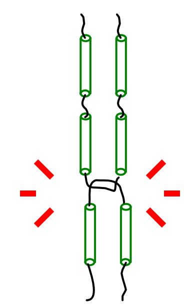


Region I
(numerous hairpins)



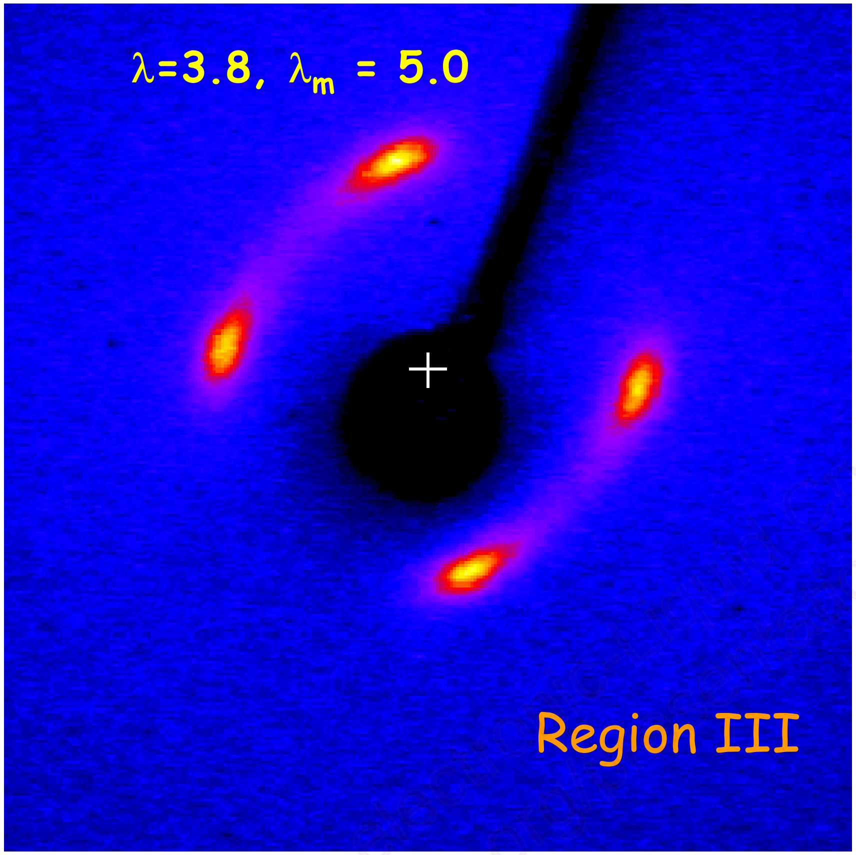
Region II (in neck)
(hairpins depleted)

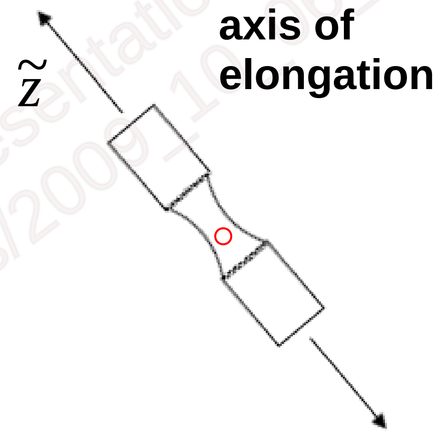
trapped hairpins?



($M_e >> M_c$)

X-ray Diffraction: Region III

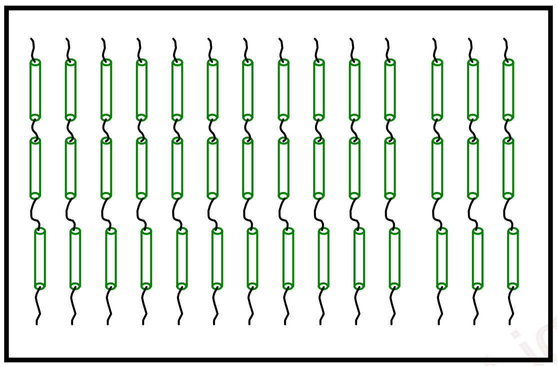




Normal (parallel) orientation of chain axes
"Layer buckling" instability

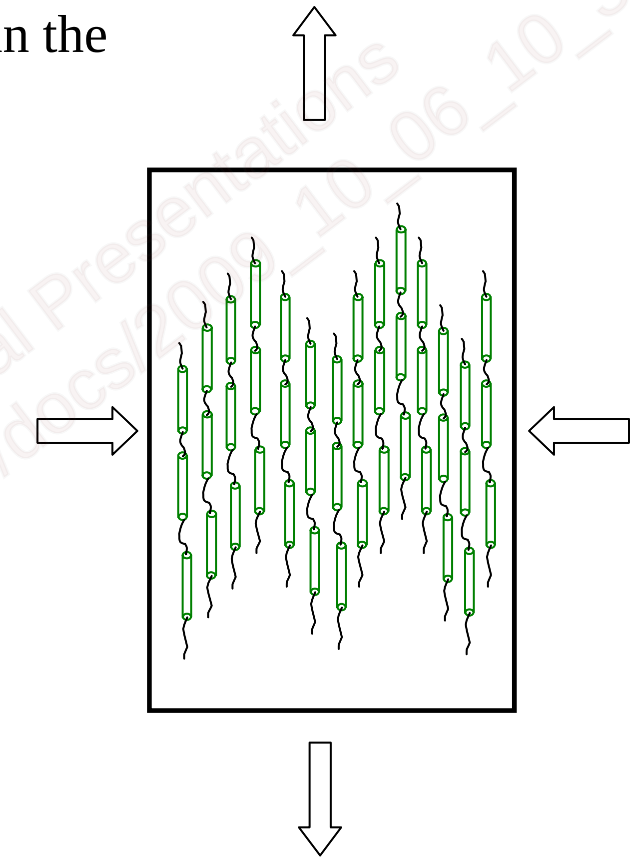
Deformation Mechanism: Layer Buckling

Increasing the stress beyond some threshold value induces layer buckling, signifying a change in the backbone conformation of the elastic chains.



Region II

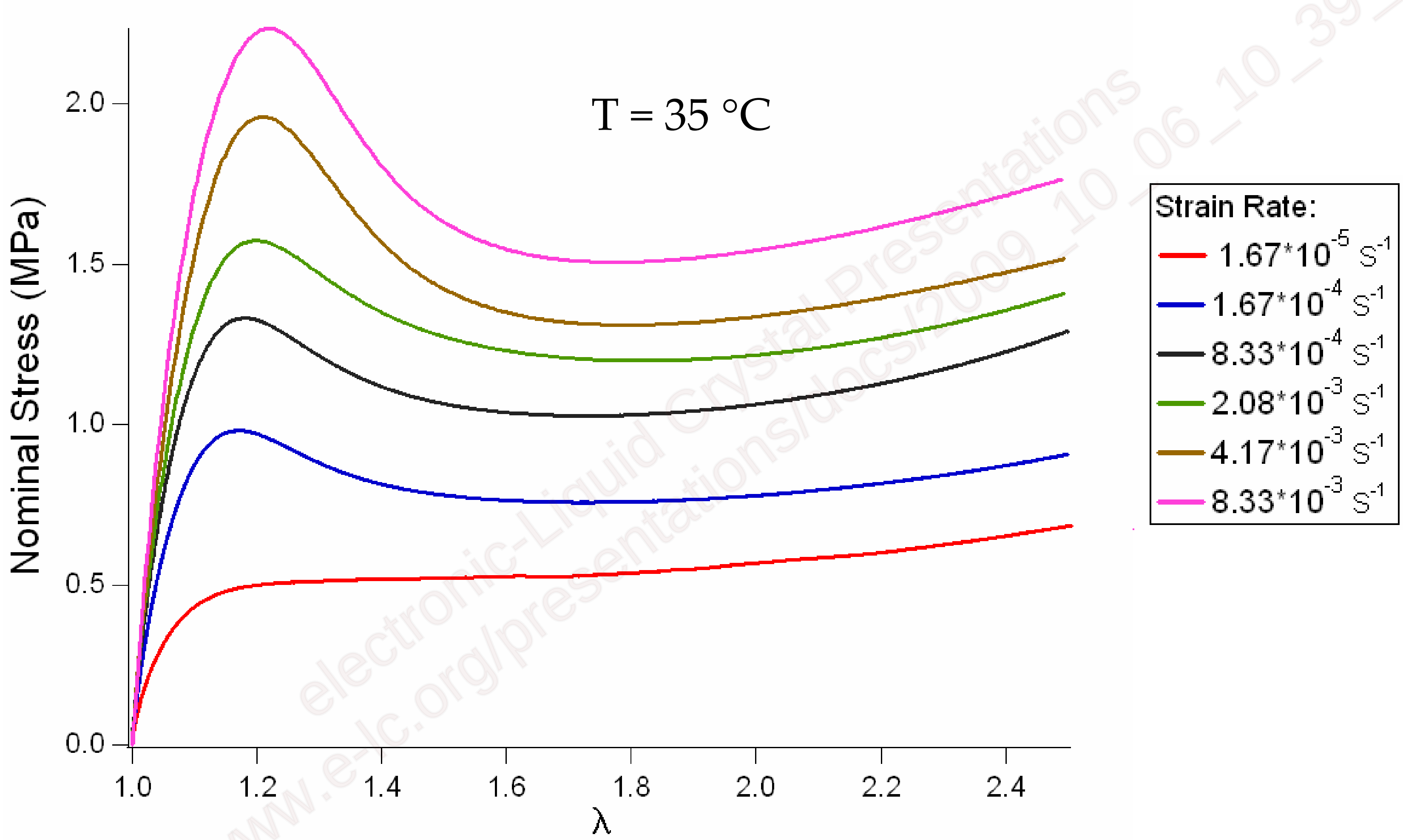
"Monodomain"



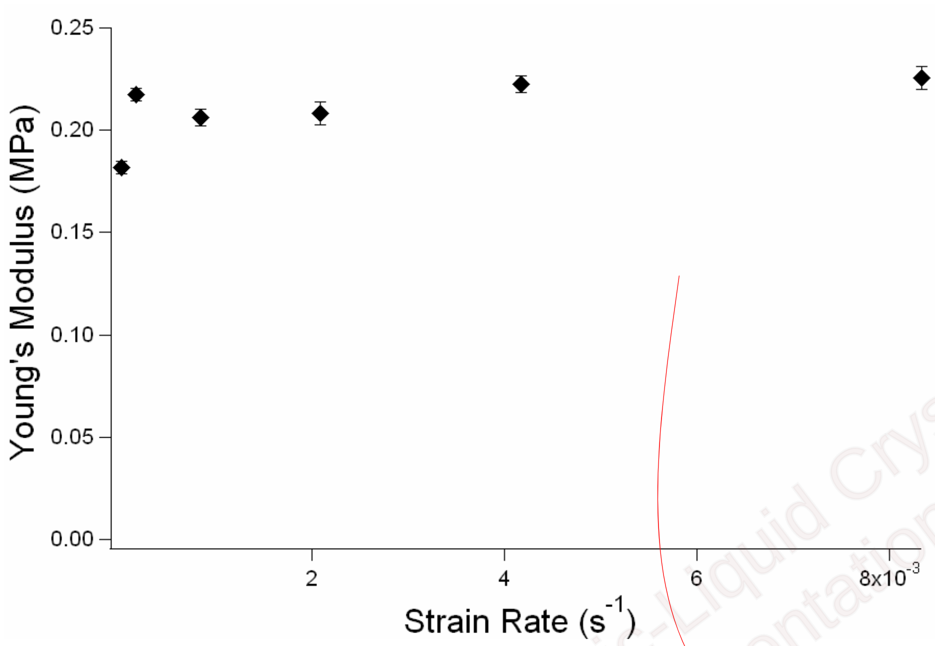
Region III:
Layer Buckling

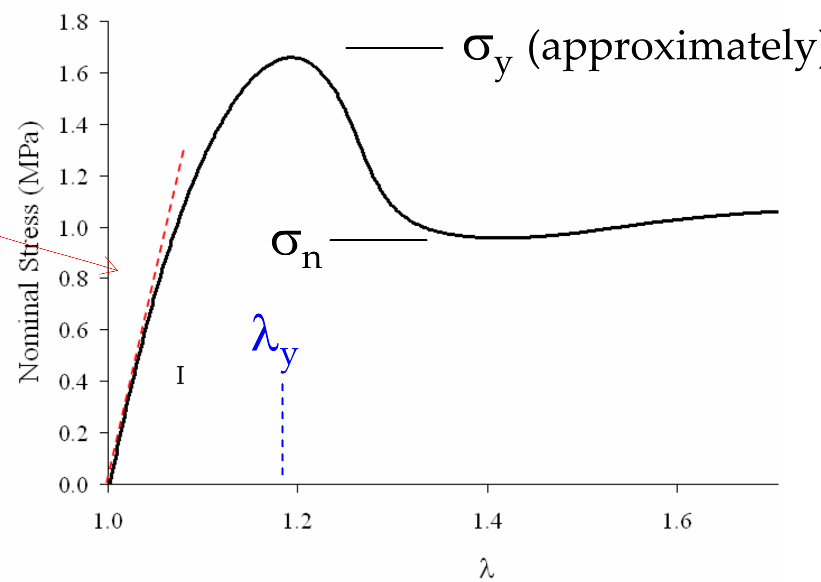
Layer buckling may also be observed in Region II at higher elongation rate / lower temperature

Mechanical Response: Effects of Strain Rate



Effects of Strain Rate on Modulus (before necking)



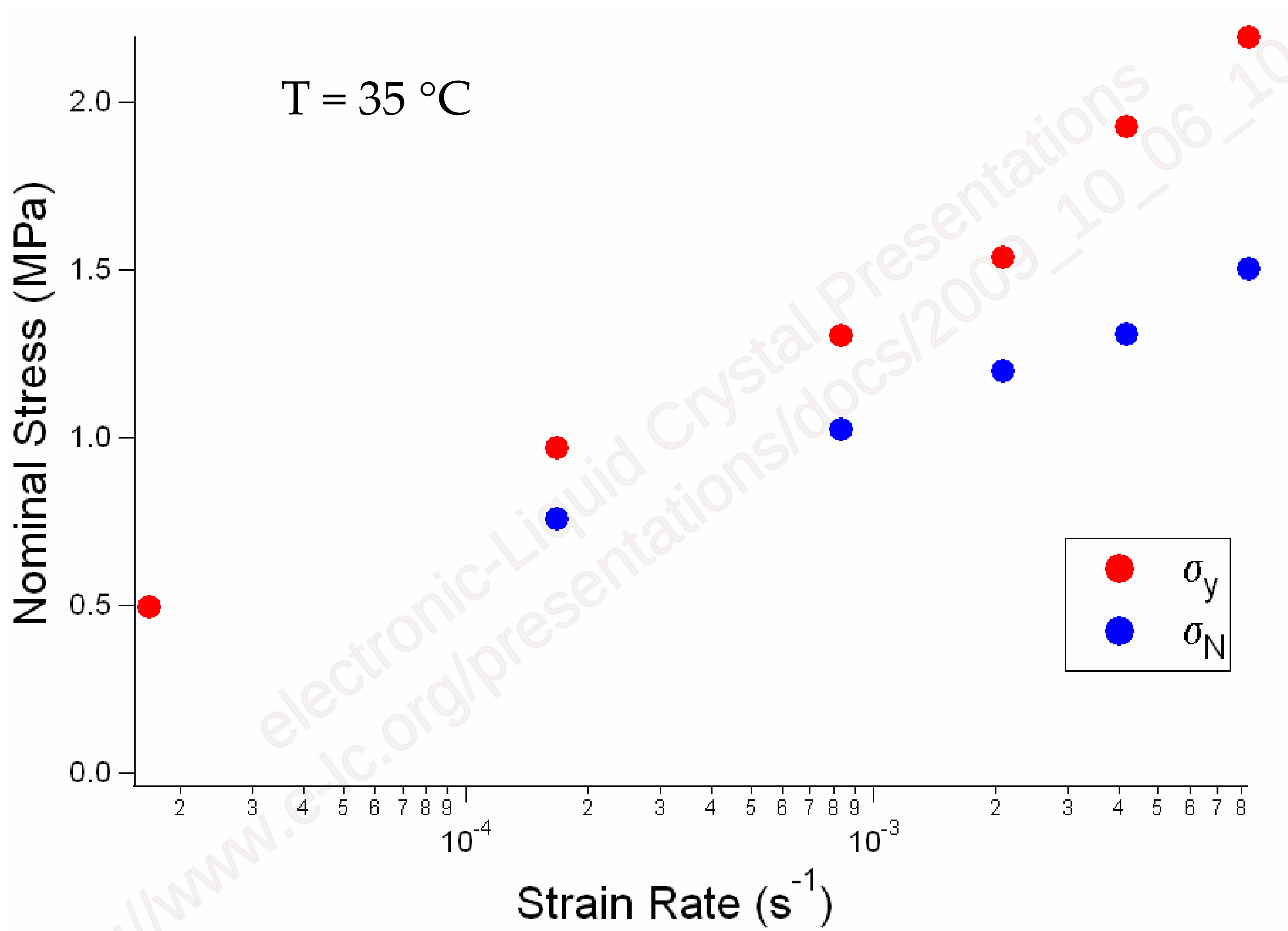


T = 35 °C

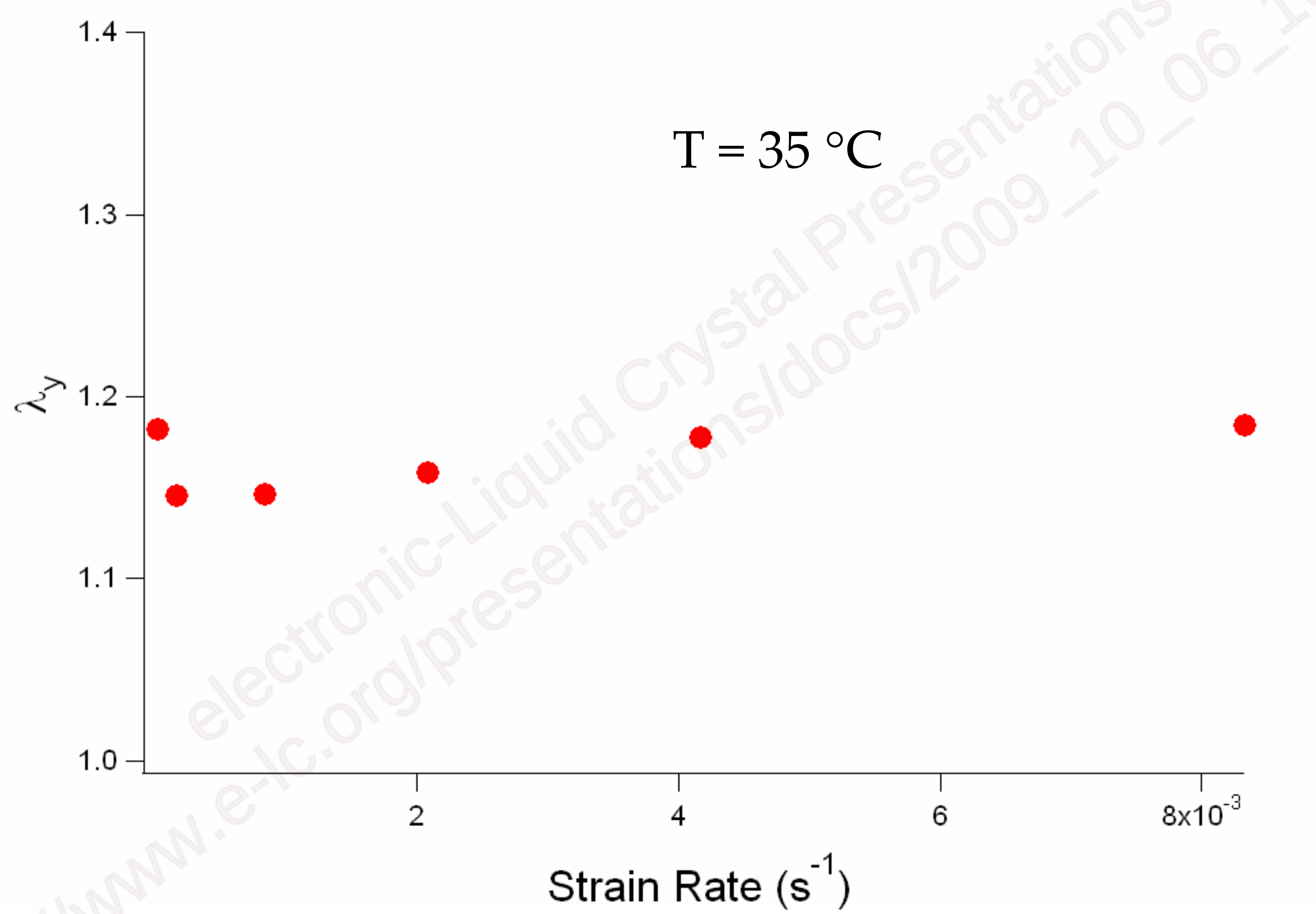
σ_y yield stress (nominal)

σ_n "necking stress"

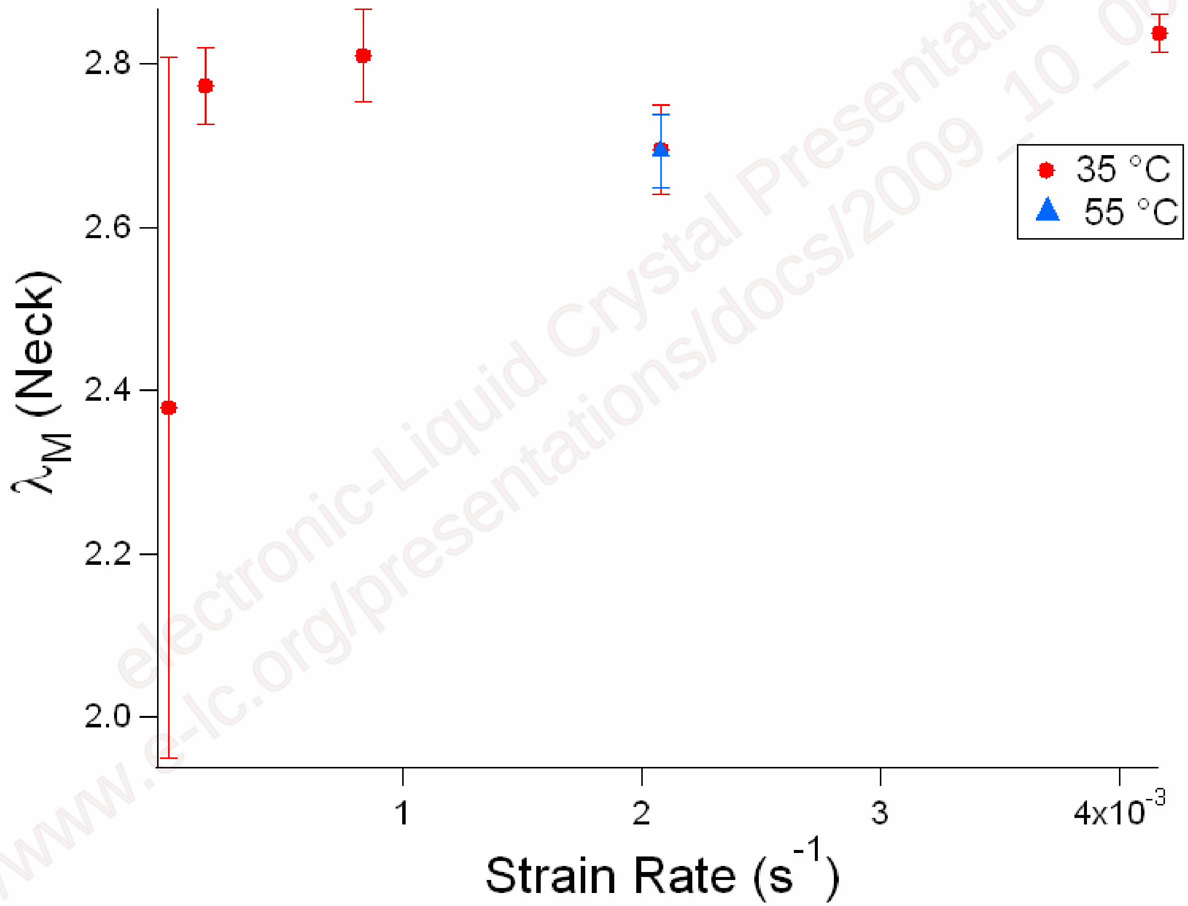
Effects of Strain Rate on σ_y and σ_n



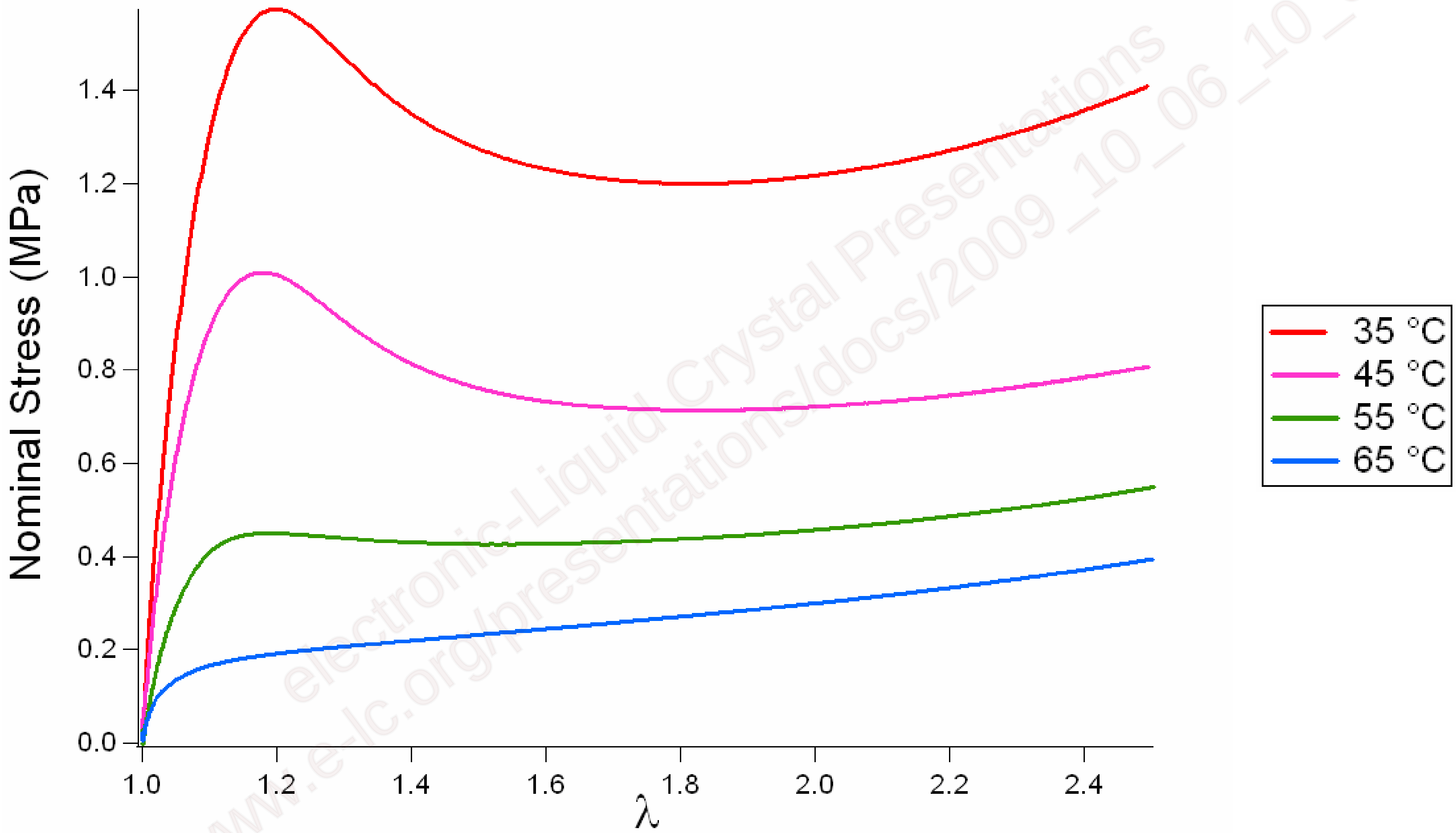
Dependence of Yield Strain on Stain Rate



Natural Draw Ratio?

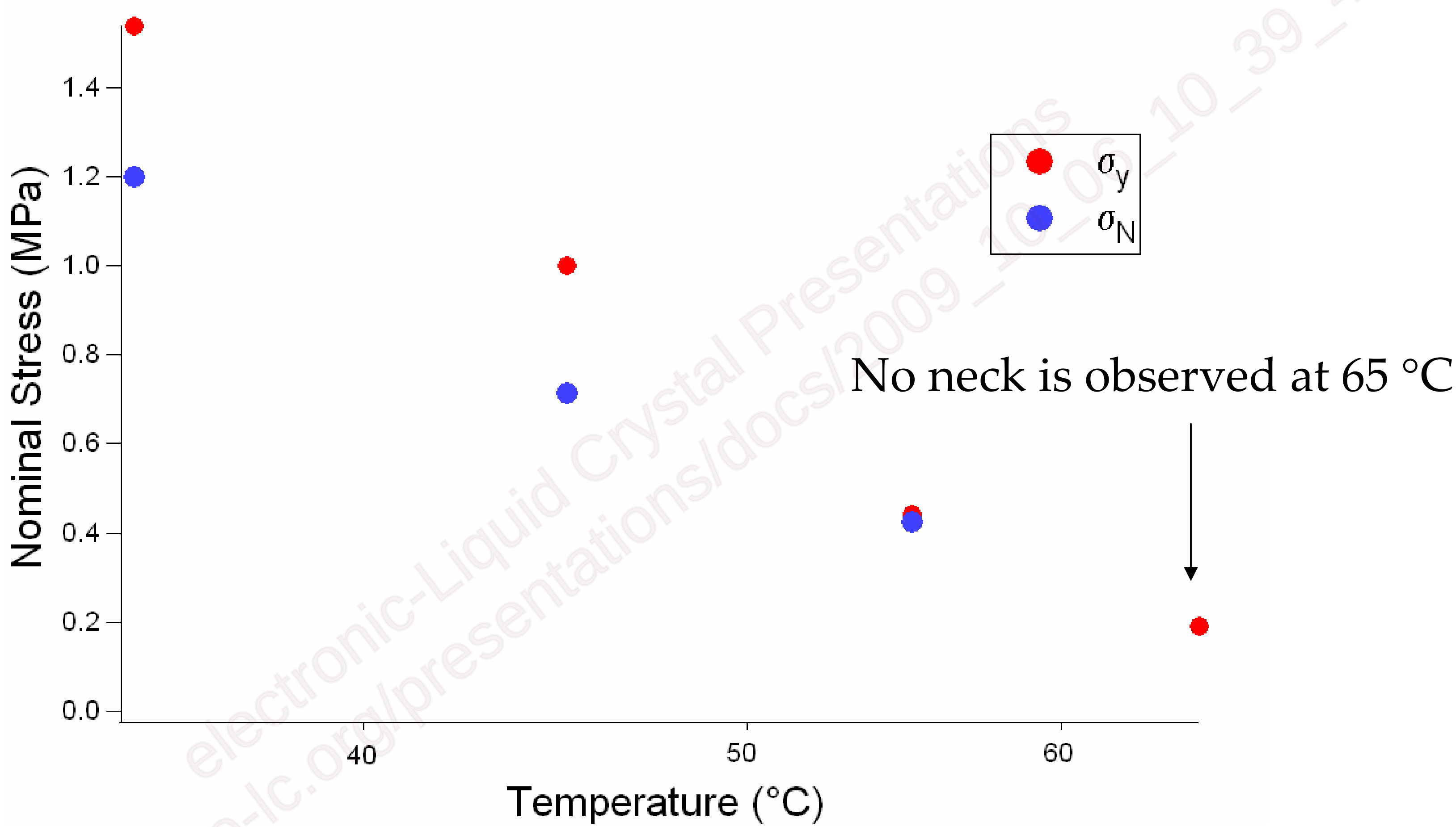


Mechanical Response: Effects of Temperature



constant strain rate of $2.08 \cdot 10^{-3}$ s^{-1}

Effects of Temperature on σ_y and σ_n



constant strain rate of $2.08 \cdot 10^{-3}$ s^{-1}

Conclusions: Necking in Main-Chain LCE

- Necking is a spatially inhomogeneous manifestation of the P-M transition in smectic MCLCE
- Conformational transition: hairpinned coils to extended chains
- Geometrical reduction in cross-sectional area upon loss of first hairpins enhances stress locally, promoting instability
- System is more prone to instability at lower temperatures, higher elongation rates (high Deborah number)

Remaining Questions

- Adiabatic heating at neck significant in smectic MCLCE?
- Necking is possible in nematic MCLCE?

Acknowledgment

Prof. O. Lavrentovich - helpful discussions regarding S_{CA} phase

Support

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