Shear-induced onion formation of complex bilayer lamellar phase

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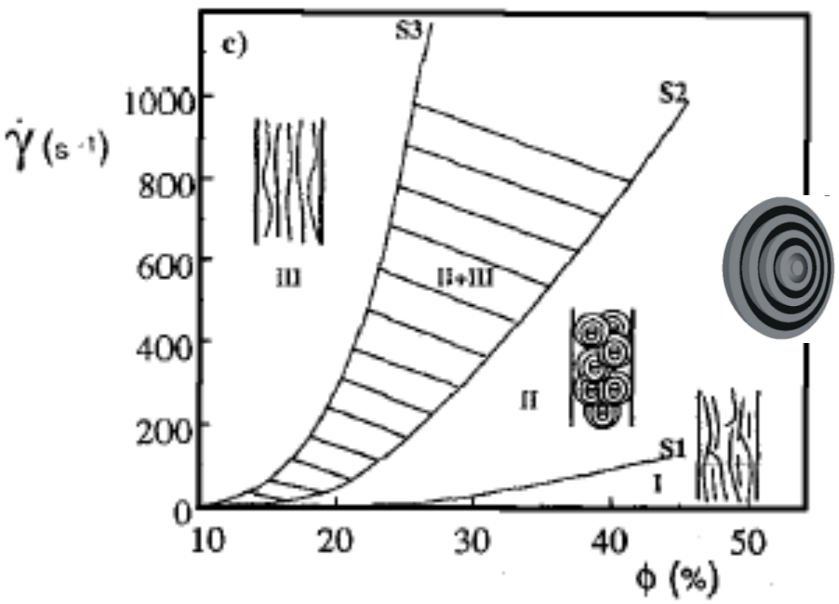
Shear induced onion phase



SDS / Dodecane / Pentanol / Water System

O. Diat, D. Roux, F. Nallet, (1993)

Mesoscopic structure

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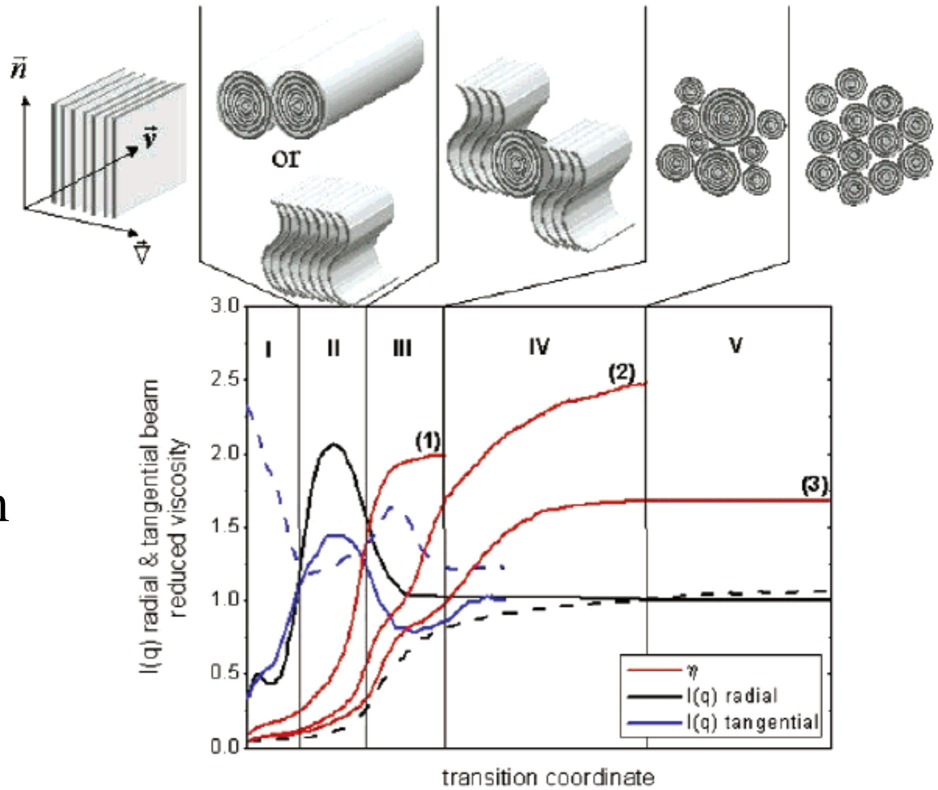
Rheology of L_α phase

L_α ➡ Cylinder / Buckled L_α ➡ Onion



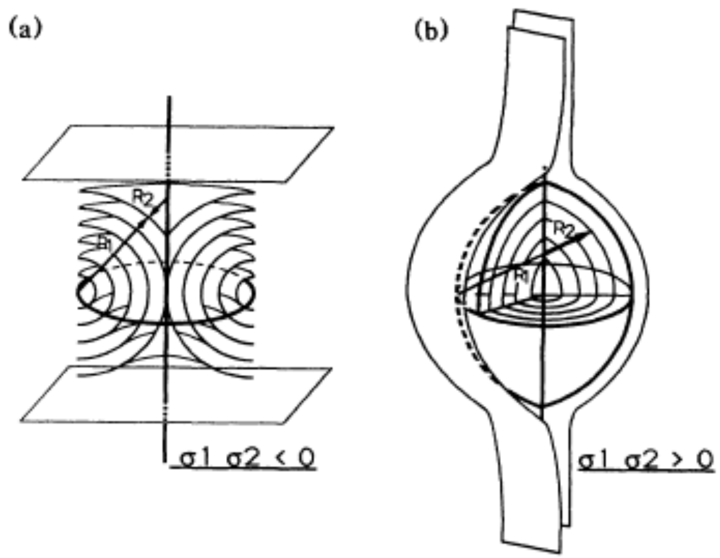
$C_{10}E_3/H_2O$ system

Rheometry + SANS

W. Richtering, *et al.*, (2003)

Onion is defects ?

Focal Conic Domain



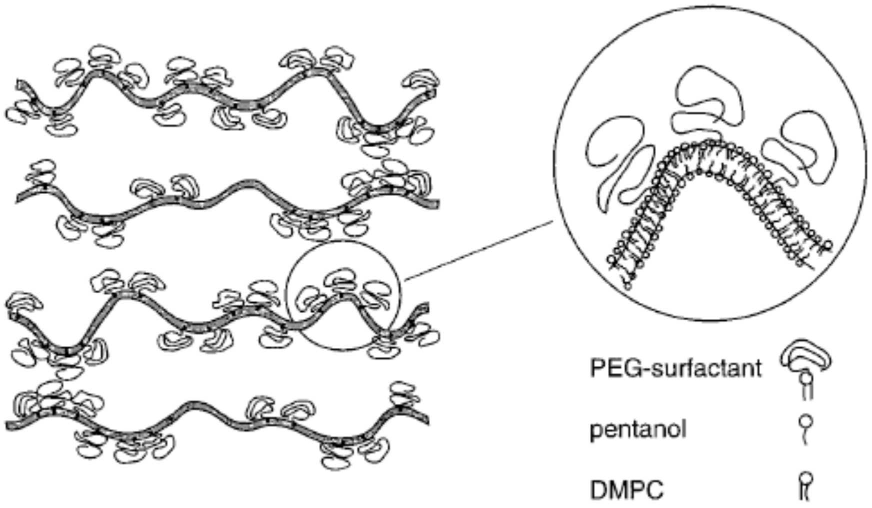
FCD I FCD II

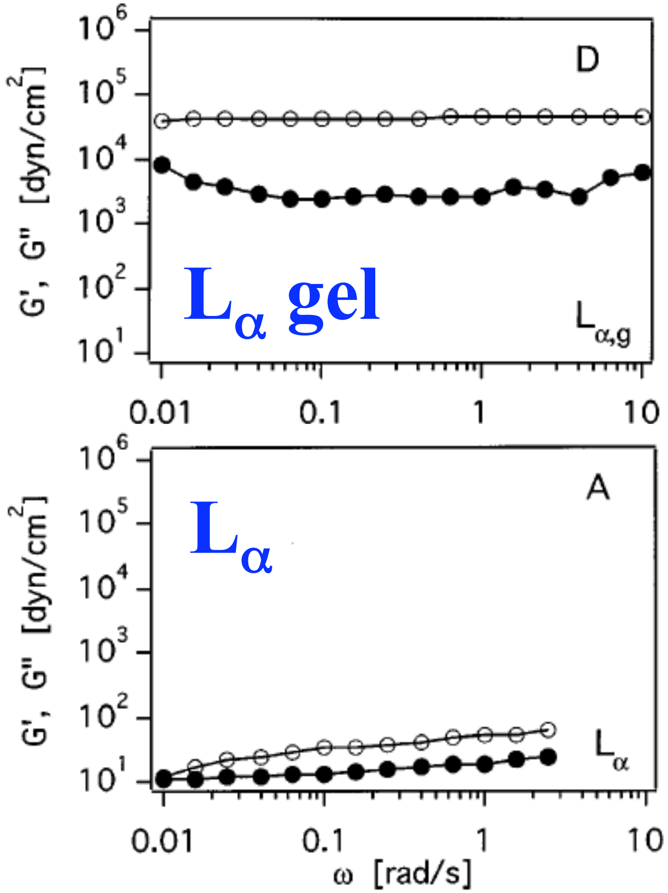
Oily streak defect Onion

What is difference between defect and onion ?

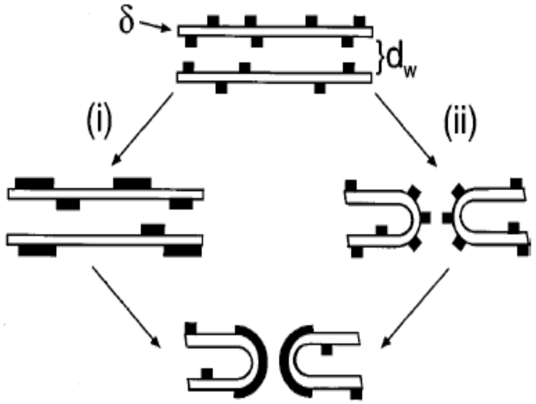
Rheology of lamellar phase modified by polymer

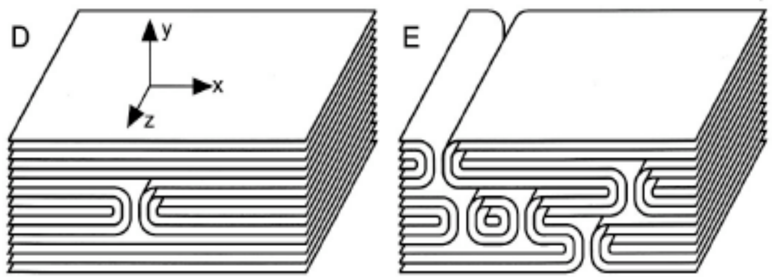
H. E. Warriner, *et al.*, (1997)

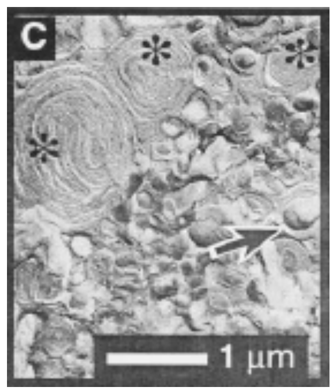




Segregation of polymer chains

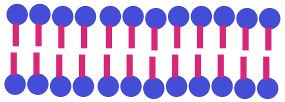






Defect-induced gelation

Complex bilayer lamellar phase



C_iE_j nonionic surfactant

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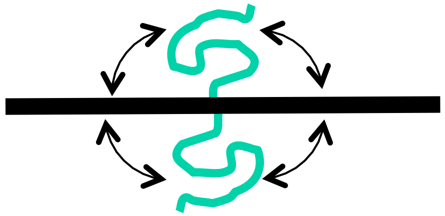
Guest component



Repulsive force due to the exclusive volume effect

Increase of the effective bilayer thickness

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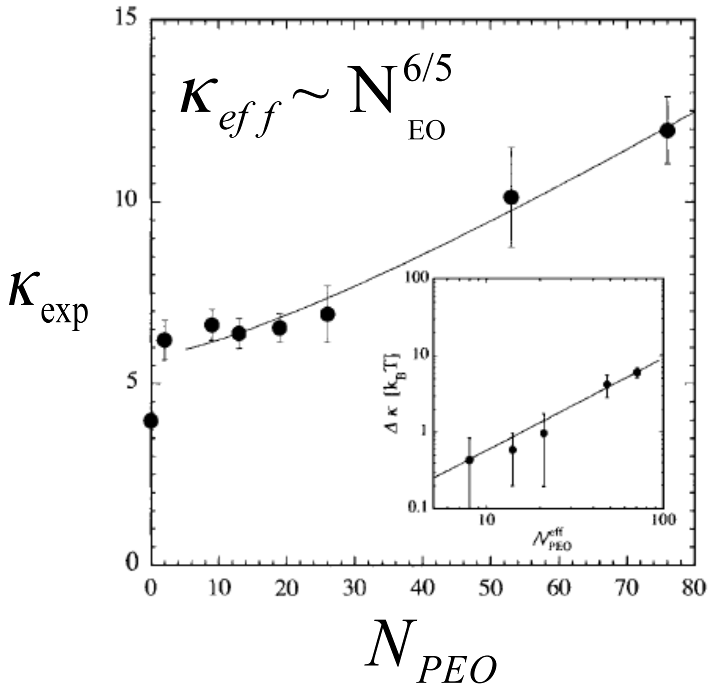
Increase of the bending rigidity
(in microscopic scale)

$$\kappa_{eff} = \kappa + 0.64 k_B T \sigma_\rho R_g^2$$

T. Taniguchi

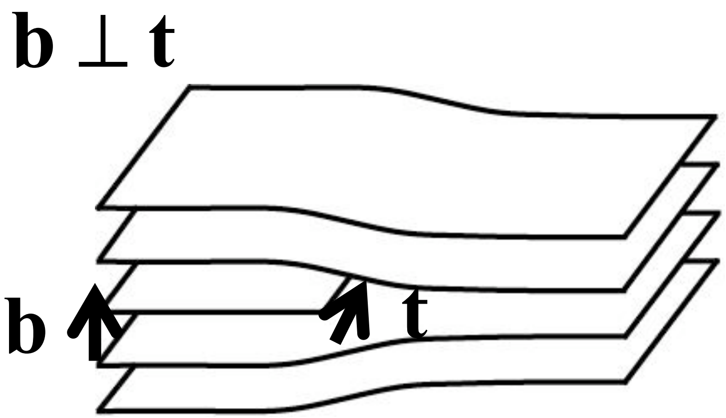
$C_{12}E_5$/Pluronic/H_2O



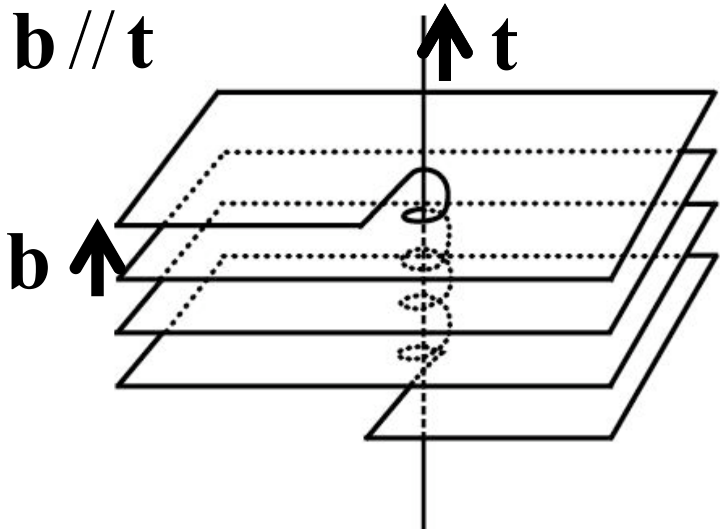
M. Imai, *et al.*, JCP (2006)

Dislocations in Smectic LC

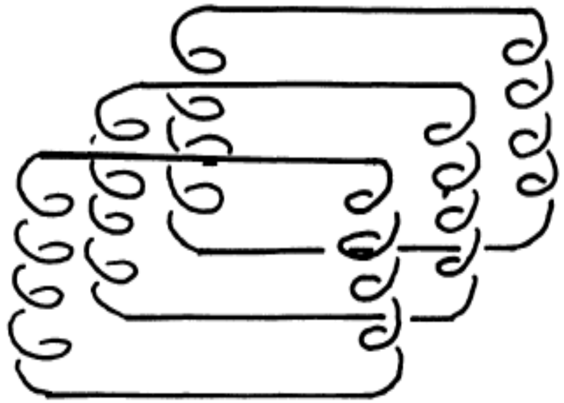
Edge dislocation

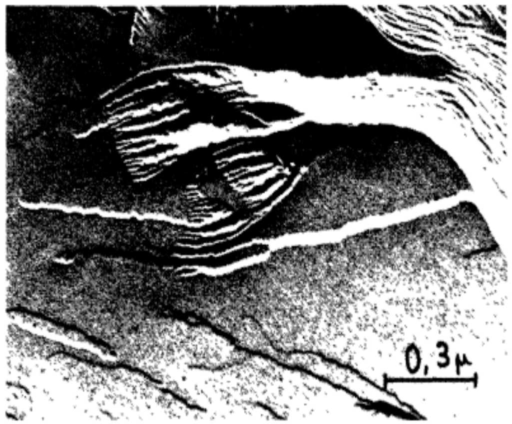


Screw dislocation



Edge and Screw dislocations form loops.





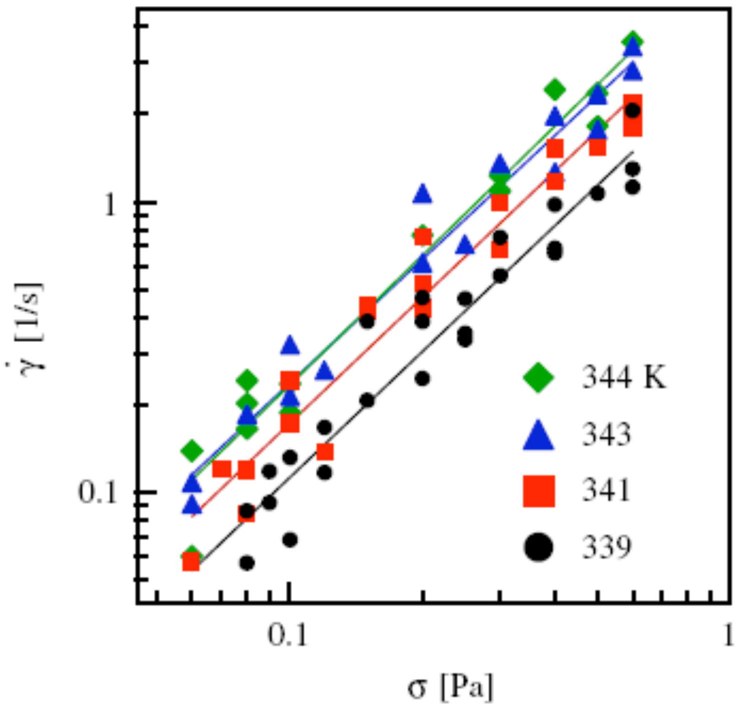
Defect-mediated rheology of Sm*A*

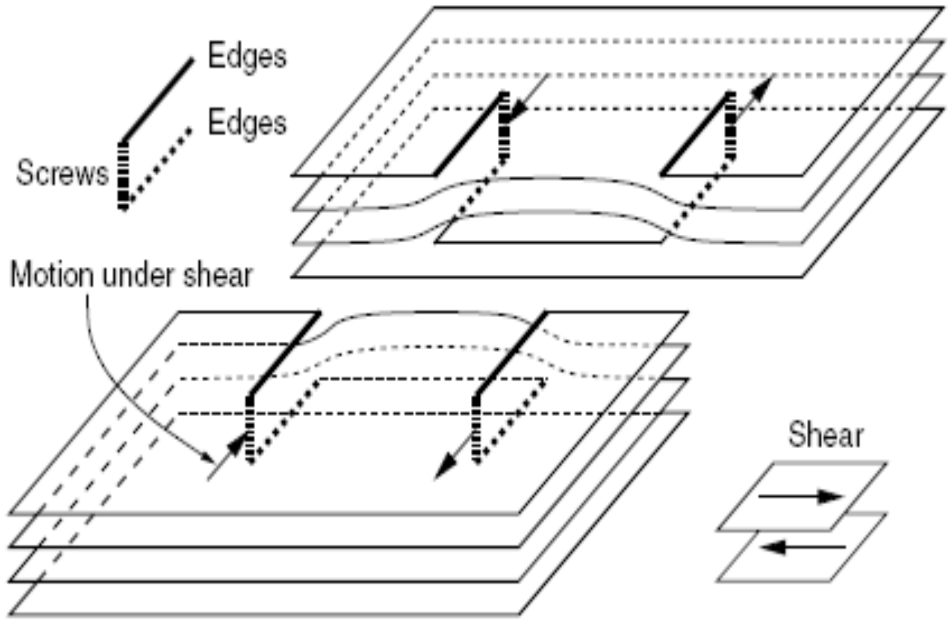
- **Shear-thinning behavior** $\dot{\gamma} \sim \sigma^m \quad m > 1$

Surfactant lyotropic lamellar phase

$C_{12}E_5$ (35wt%)

C.-Y. D. Lu, *et al.*, EPJE (2008)





$$\eta \sim \dot{\gamma}^{1/3}$$

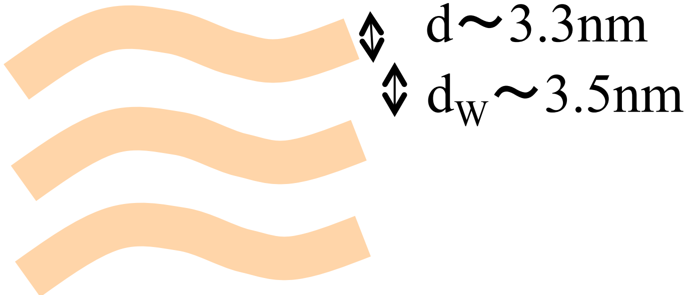
$$\dot{\gamma} \sim \frac{\mu_e}{B^{1/2}} \sigma^{3/2} \qquad \text{m=1.5}$$

Sample

Nonionic surfactant : $C_{10}E_3$

Tri-ethyleneglycol mono-*n*-decyl ether

Concentration 40wt%



Polymer mole fraction

$$X_P = \frac{n_{Poly}}{n_{C10E3} + n_{Poly}} \quad (= 6.87 \text{ x } 10^{-3} \text{ mol})$$

$$X_P = 0.2 - 1.5 mol\%$$

Pluronic（triblock copolymer）

$$EO_{N_{EO}} - PO_{N_{PO}} - EO_{N_{EO}}$$

$$R_g = 0.1078 M_{PEO}^{0.635}$$

B. Cabanne, *et al.*, (1993)

Degree of polymerization

$$N_{EO} = 3 \sim 37$$

$$N_{PO} = 30, 60$$

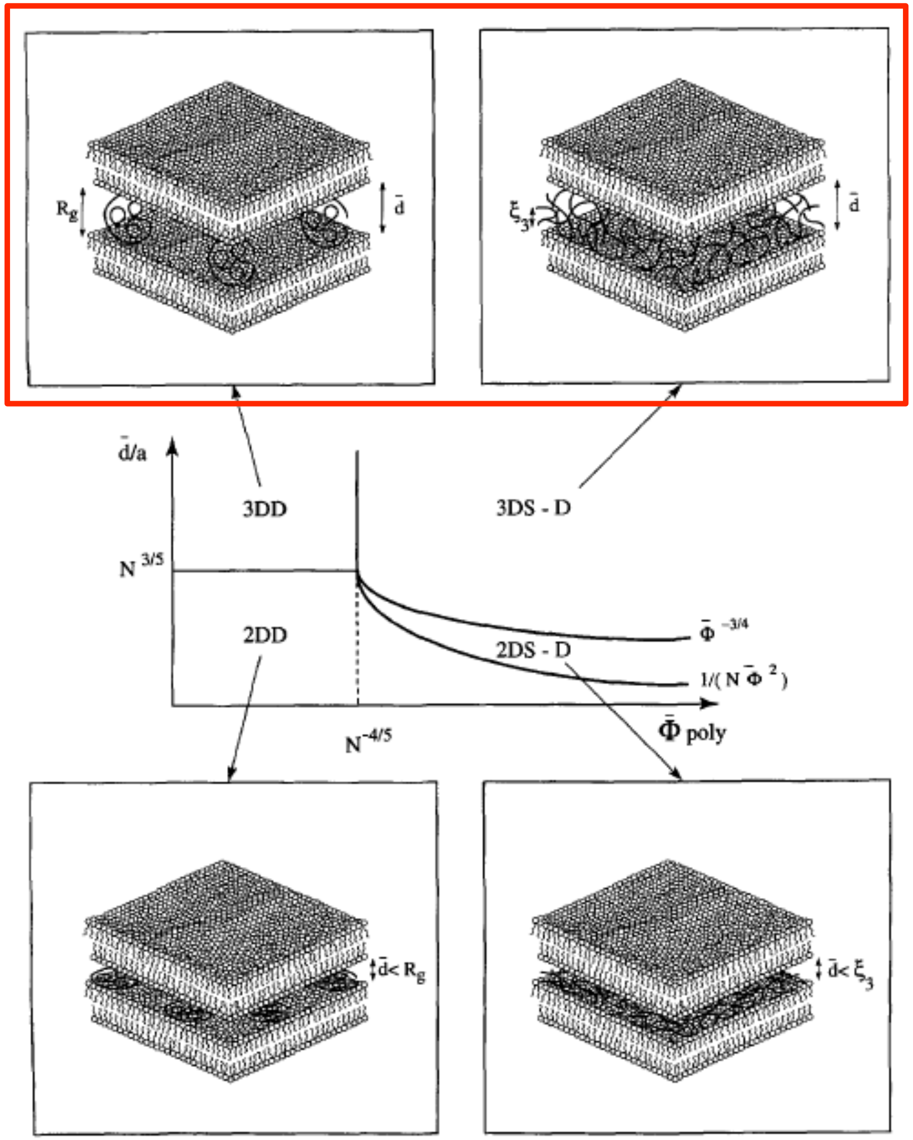
Different confinement regime of polymer in the water layer

C. Ligoure, *et al.*, (1997)

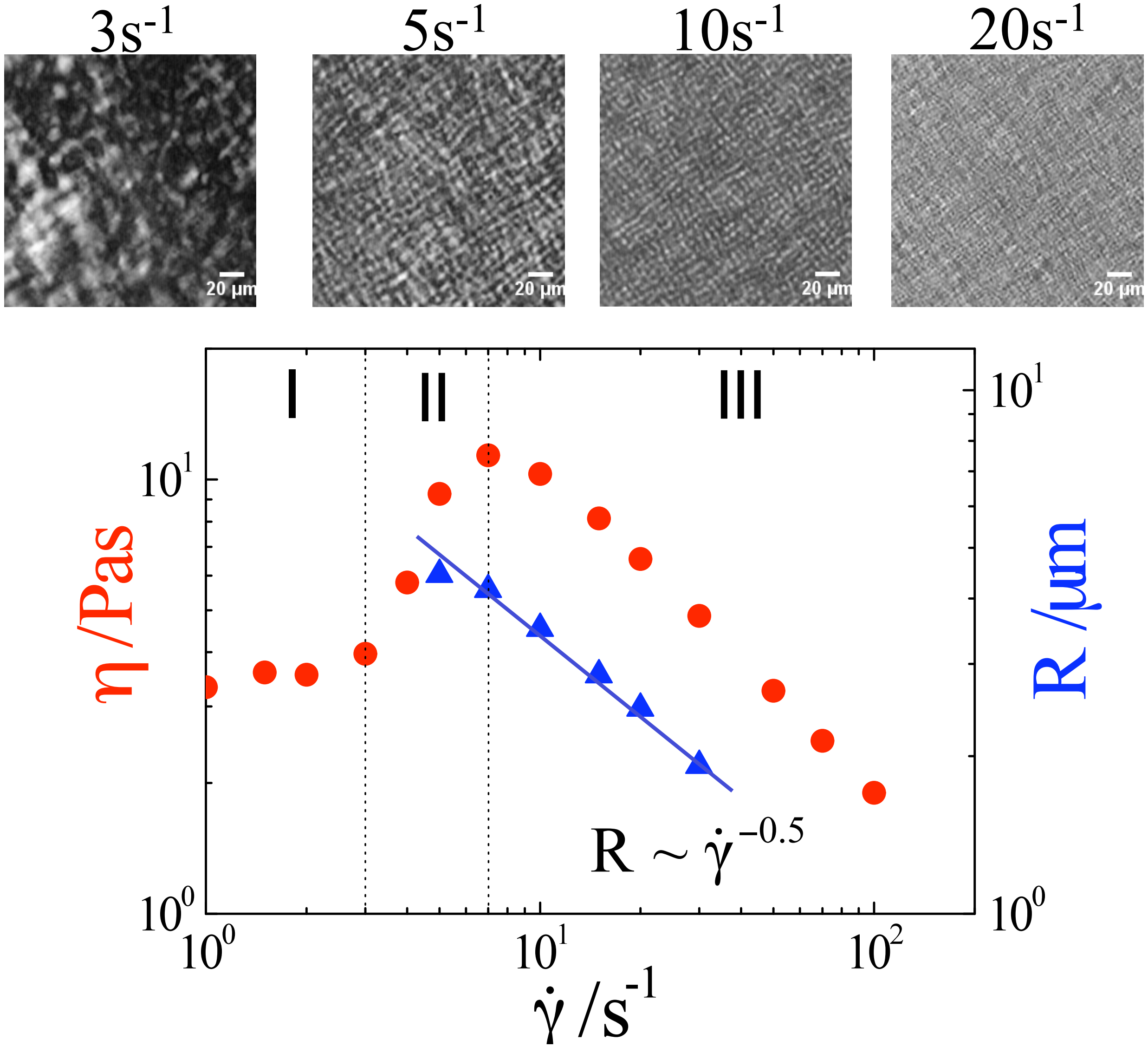
$N_{EO} = 37$ $X_P = 0.2 mol\,\%$ $1.1 mol\,\% \approx c^*$

$R_g = 1.2 nm$

$d_W = 3.5 nm$

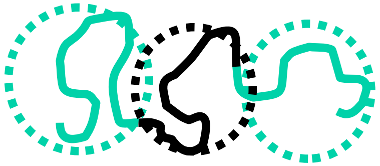


Shear rate dependence of viscosity ($C_{10}E_3/H_2O$)



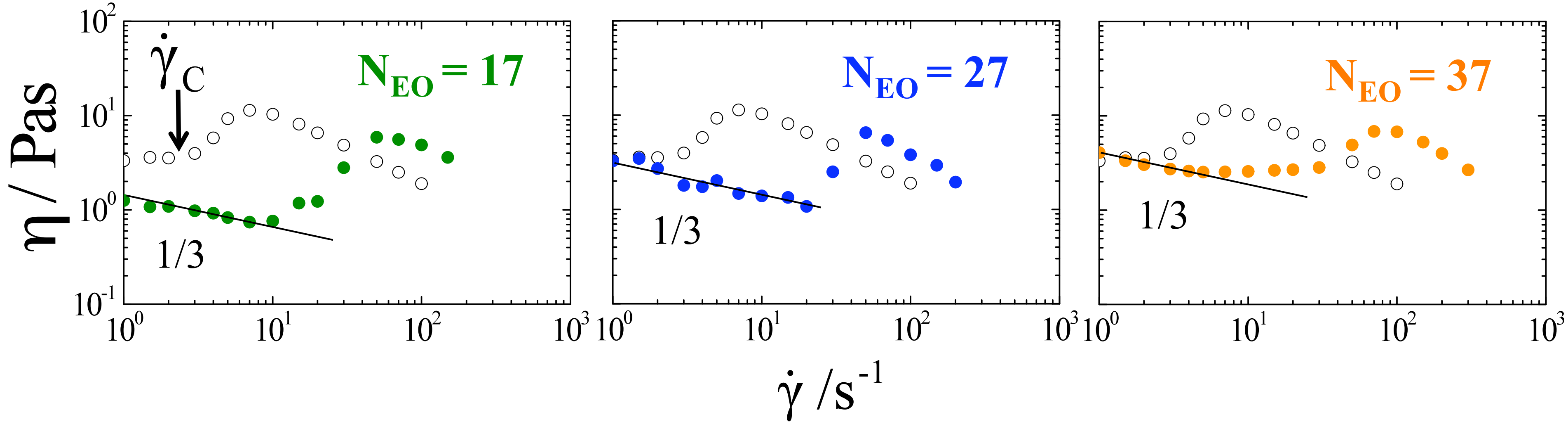
Shear-thickening is a sign of the onion formation.

$C_{10}E_3$ / Pluronic (X_P=1mol%) / H_2O system



N_{EO} = 17, 27, 37

N_{PO} ~ 60



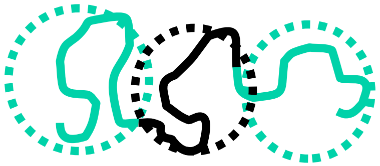
Increasing N_{EO} hinders shear induced onion formation.

Shear thinning behavior at low shear rates,

$$\eta \sim \dot{\gamma}^{1/3}$$

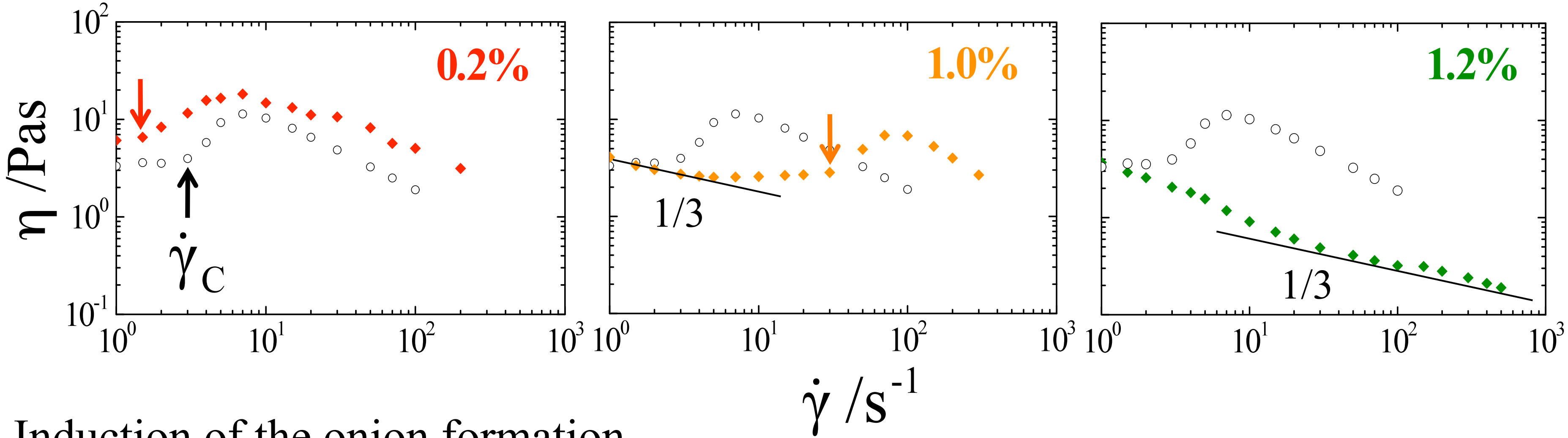
Shear thinning behavior … dislocation loop motion

Polymer concentration dependence of L_α/Onion transition



$N_{EO} = 37$, $R_g = 1.2$ nm
$N_{PO} = 60$, $R_g = 1.8$ nm

Pluronic P105 (c*=1.1mol%)



Induction of the onion formation

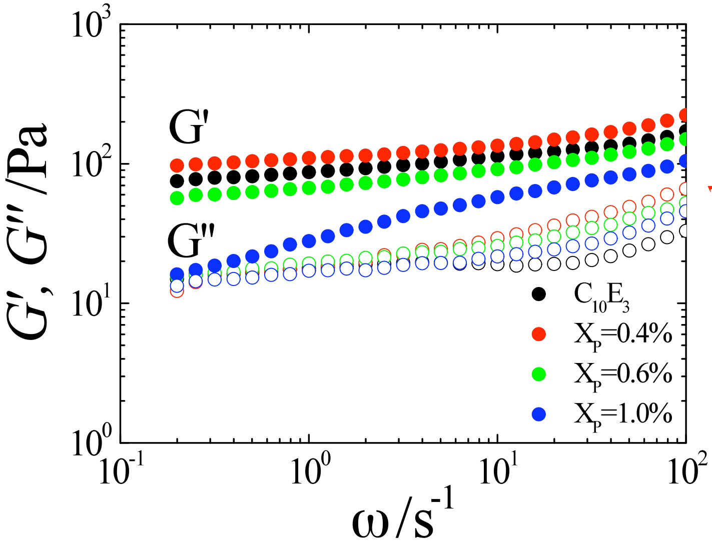
Inhibition of the onion formation

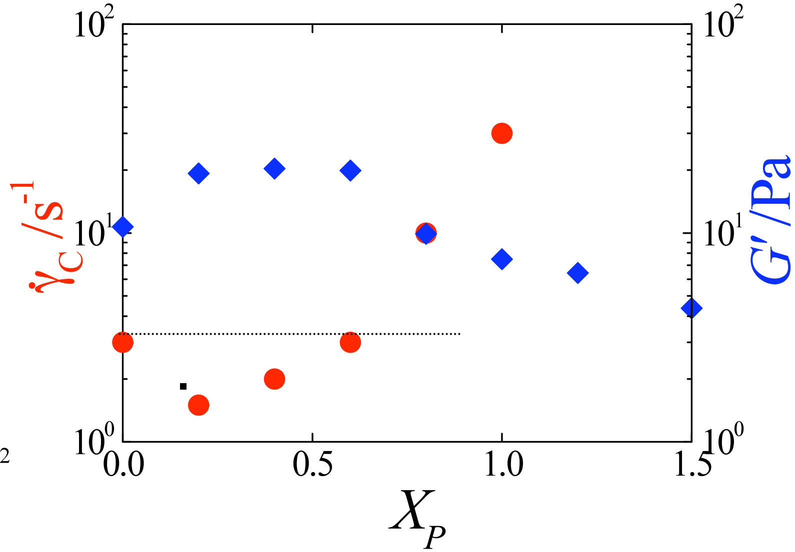
No Onion formation

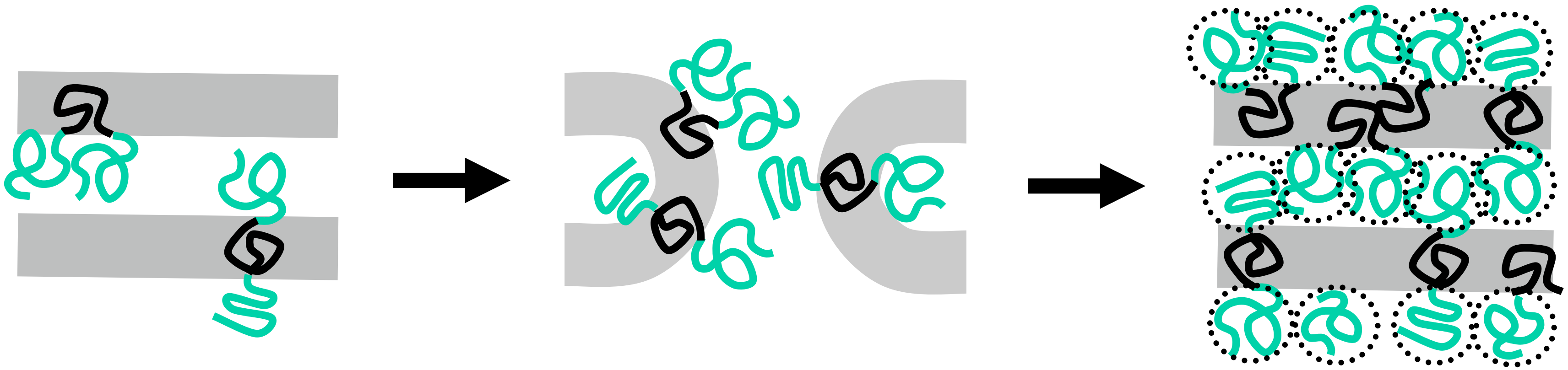
At low polymer concentration,
the onion phase is easily induced by shear.

Viscoelasticity of polymer-doped lamellar phase

G’ and G’’ measurements after pre-shear at 1s^{-1} (in the lamellar phase)



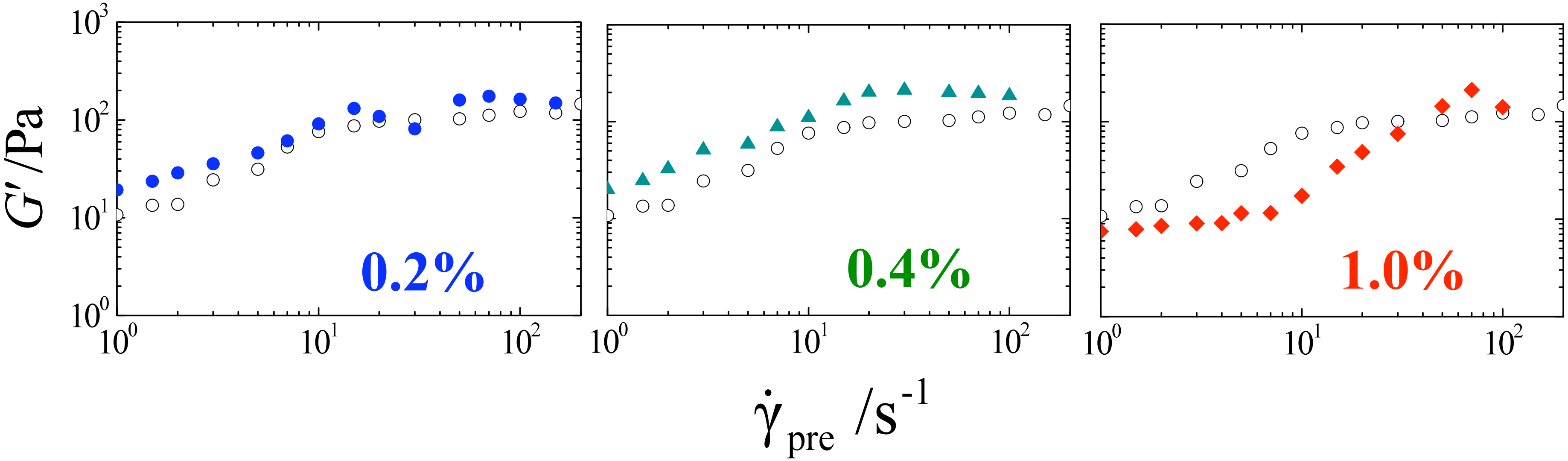




Polymer segregation (inhomogeneous distribution) on the membrane causes the increase in the defects density.

High viscoelasity gives the Onion formation.

Development of modulus with pre-shear

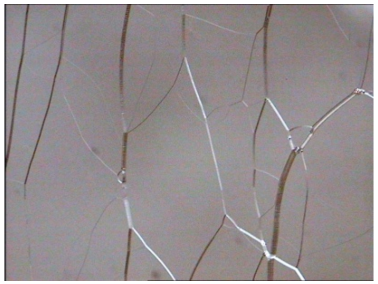


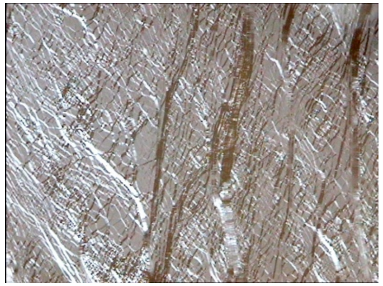
Shear modulus develops with pre-shear rate.

$C_{10}E_3/H_2O$

Conc.=40wt%

Gap = 50μm

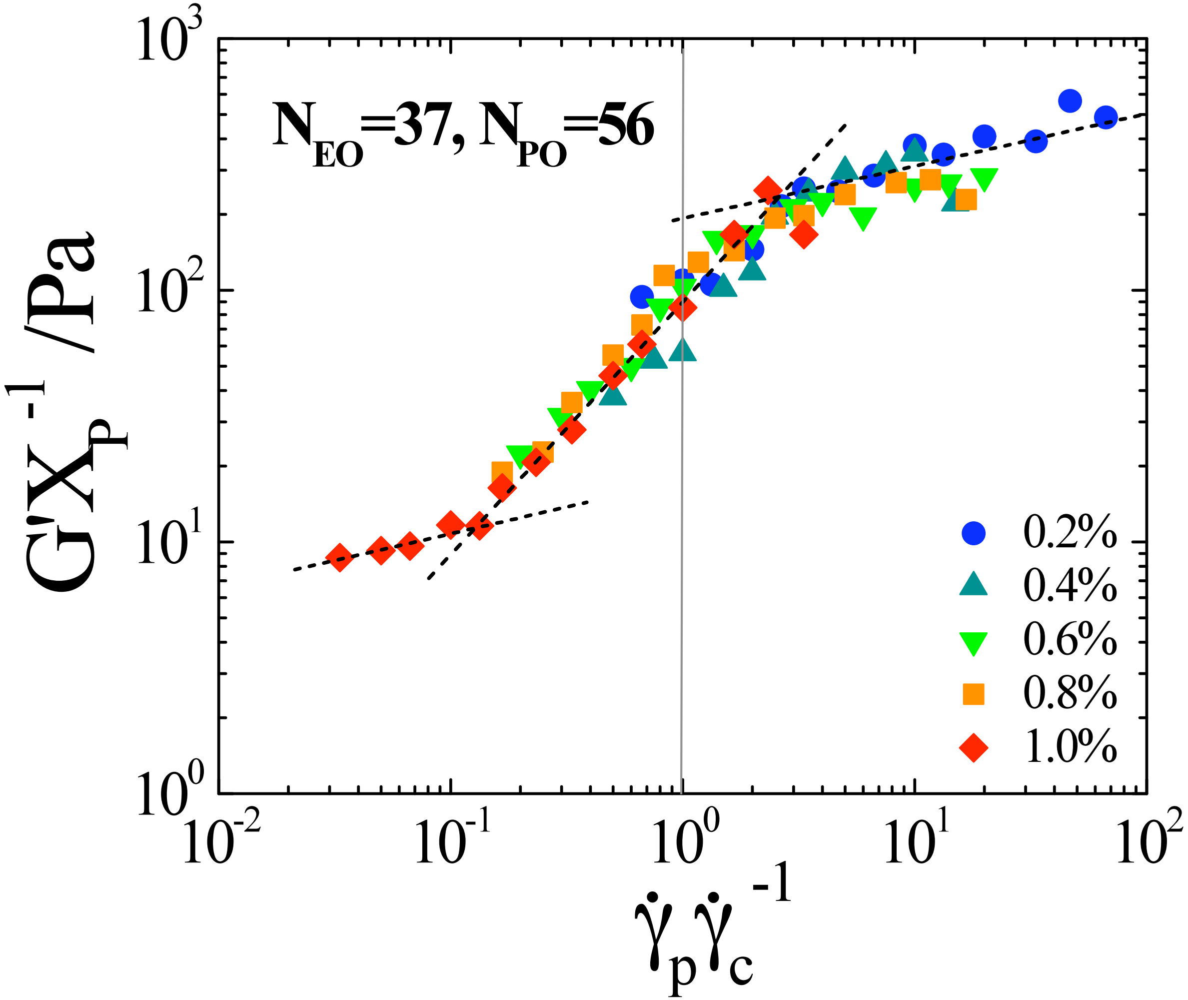




Defect density increases with shear.

$$\rho = \rho(\dot{\gamma}_{pre}, X_{Poly}) \qquad G' = G'(\dot{\gamma}_{pre}, X_{Poly})$$

Viscolasticity of lamellae/onion transformation process

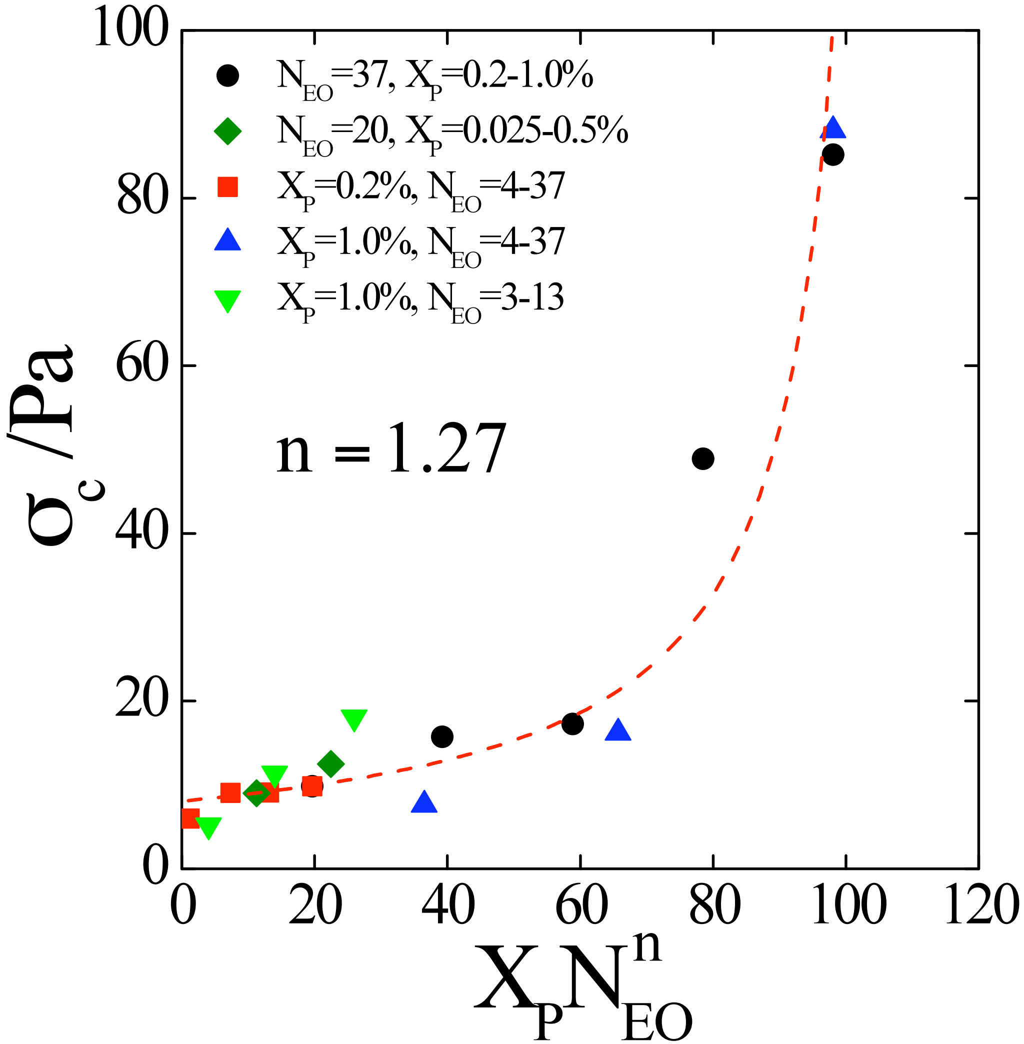


Onion formation is controlled by defect density ?

G' starts to increase at the tenth of the critical shear rate.

Bending modulus and Critical shear stress

$$\kappa_{eff} = \kappa + 0.64 k_B T \sigma_\rho R_g^2$$



$$R_g = 0.1078 M_{PEO}^{0.635}$$

$$\sigma_c \sim (x_c - x)^{-1}$$

$$x = X_P N_{EO}^n$$

$$x_c = 107$$

$X_P = 1.09$ mol%
c* = 1.1 mol%

At X_P=1mol%,

$N_{EO} = 49$
$R_g = 1.6$ nm

Critical shear stress can be scaled by the increment of the bending modulus.

Summary

Shear induced onion formation can be controlled by polymer.

Defect formation triggers the onion formation.

Defect density depends on the polymer concentration.

Defect density increases with pre-shear.

Shear stress controls the shear induced onion formation behavior.