Shear-induced onion formation
of complex bilayer lamellar phase

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Shear induced onion phase

SDS / Dodecane / Pentanol / Water System


Mesoscopic structure

Rheology of $L_\alpha$ phase

C$_{10}$E$_3$/H$_2$O system

Rheometry + SANS

Onion is defects?

**Focal Conic Domain**

What is difference between defect and onion?
Rheology of lamellar phase modified by polymer


Segregation of polymer chains

Defect-induced gelation

\( \alpha \) gel

\( L_\alpha \)
Complex bilayer lamellar phase

$\text{C}_i\text{E}_j$ nonionic surfactant

$\text{PEO} + \text{PPO} + \text{PEO}$

Guest component

Repulsive force due to the exclusive volume effect

Increase of the effective bilayer thickness

Increase of the bending rigidity (in microscopic scale)

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

T. Taniguchi

$\kappa_{eff} \sim N_{EO}^{6/5}$

Dislocations in Smectic LC

Edge dislocation

\[ b \perp t \]

Screw dislocation

\[ b \parallel t \]

Edge and Screw dislocations form loops.
Defect-mediated rheology of SmA

- Shear-thinning behavior

Surfactant lyotropic lamellar phase

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

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

$\dot{\gamma} \sim \sigma^m$  $m > 1$

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

Sample

Nonionic surfactant: C\textsubscript{10}E\textsubscript{3}
Tri-ethyleneglycol mono-\textit{n}-decyl ether

Concentration 40wt\%

\[d \sim 3.3\text{nm}\]
\[d_{w} \sim 3.5\text{nm}\]

Pluronic (triblock copolymer)

\[\text{EO}_{N_{EO}} - \text{PO}_{N_{PO}} - \text{EO}_{N_{EO}}\]

Polymer mole fraction

\[X_{P} = \frac{n_{Poly}}{n_{C10E3} + n_{Poly}} (= 6.87 \times 10^{-3}\text{ mol})\]

\[X_{P} = 0.2 - 1.5\text{ mol\%}\]

Degree of polymerization

\[N_{EO} = 3 \sim 37\]
\[N_{PO} = 30, 60\]

B. Cabanne, \textit{et al.}, (1993)
Different confinement regime of polymer in the water layer


\[ N_{EO} = 37 \]
\[ X_p = 0.2 \text{mol} \% \]
\[ R_g = 1.2 \text{nm} \]
\[ d_W = 3.5 \text{nm} \]
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 ($X_p=1\text{mol}\%$) / H$_2$O system

$N_{EO} = 17, 27, 37$

$N_{PO} \sim 60$

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 $L_\alpha$/Onion transition

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

Pluronic P105 ($c^*=1.1\text{mol\%}$)

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 viscoelasticity gives the Onion formation.
Development of modulus with pre-shear

Shear modulus develops with pre-shear rate.

\[ G' = G'(\dot{\gamma}_{\text{pre}}, X_{\text{Poly}}) \]

Defect density increases with shear.

\[ \rho = \rho(\dot{\gamma}_{\text{pre}}, X_{\text{Poly}}) \]

\( C_{10}E_3/H_2O \)
Conc. = 40 wt%  
Gap = 50 \( \mu \)m
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.

$N_{EO} = 37, N_{PO} = 56$
Critical shear stress can be scaled by the increment of the bending modulus.

\[ \kappa_{\text{eff}} = \kappa + 0.64k_B T \sigma \rho R_g^2 \]

\[ R_g = 0.1078 M_{PEO}^{0.635} \]

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

\[ x = X_P N_{EO}^n \]

\[ x_c = 107 \]

\[ \left\{ \begin{array}{l} X_P = 1.09 \text{ mol}\% \\ c^* = 1.1 \text{ mol}\% \end{array} \right. \]

At \( X_P = 1 \text{ mol}\% \),

\[ \left\{ \begin{array}{l} N_{EO} = 49 \\ R_g = 1.6 \text{ nm} \end{array} \right. \]
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.