Rheology of Structured Fluids

Ralph H. Colby
Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

Acknowledgements:

Frank Bates
Rich Connelly
Giancarlo Galli
Jeff Gillmor
Beth Hall
Michele Laus
Lauren Nentwich
Chris Ober
Scott Clingman

LIQUID CRYSTALS

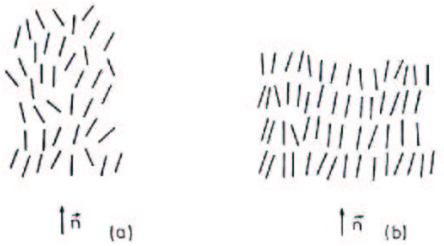


Fig. 1.1. Schematic picture of the nematic (a) and smectic A (b) phase

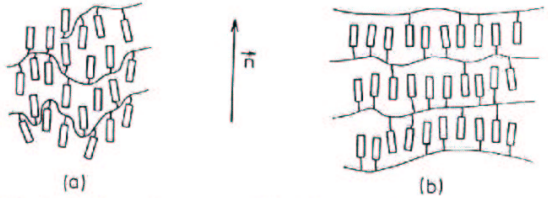


Fig. 4.4. Schematic representation of a nematic (a) and a smectic phase (b) composed of side-chain polymers

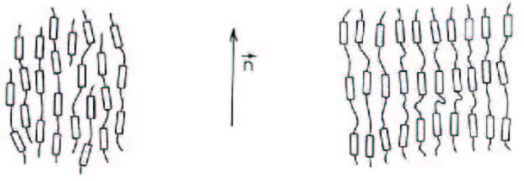
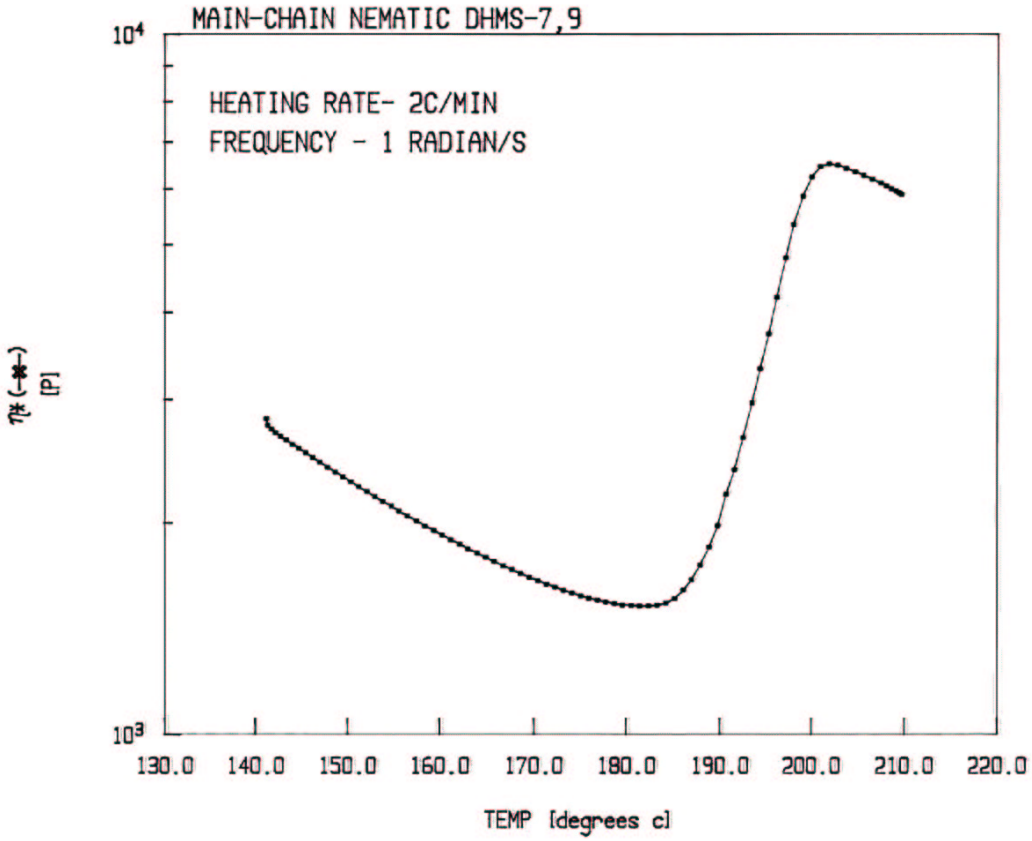


Fig. 4.2. Schematic representation of a nematic (a) and a smectic phase (b) composed of main-chain polymers



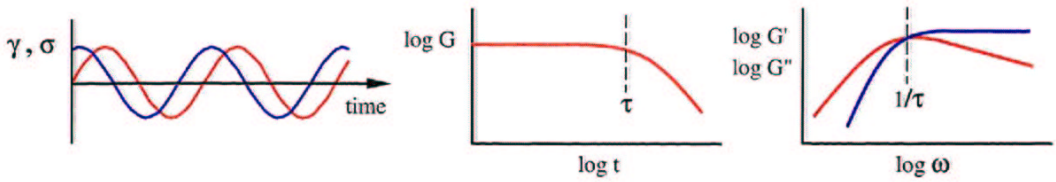
Linear Viscoelastic Experiments

1. Step Strain

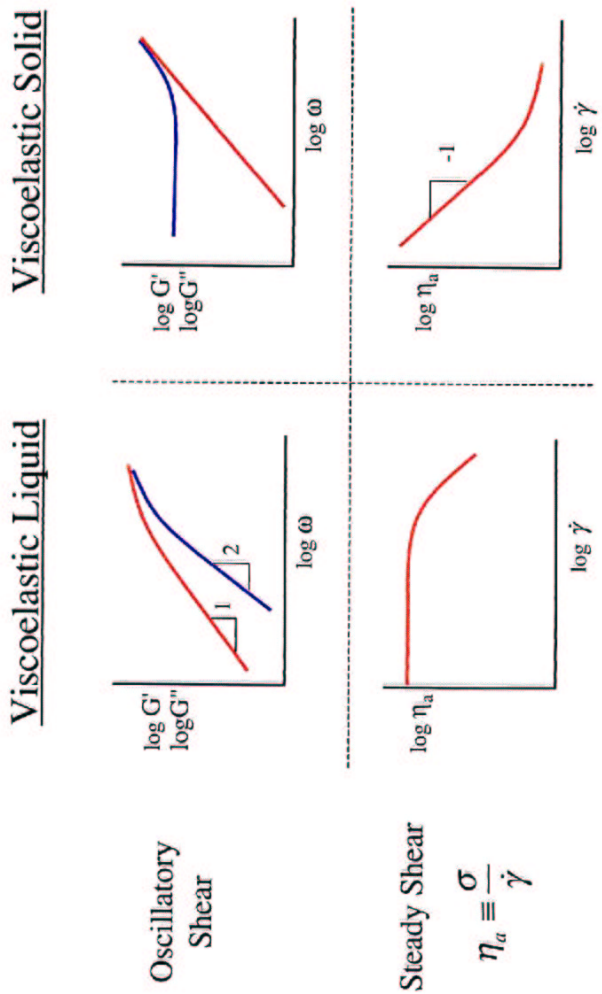
$$G(t) \equiv \frac{\sigma(t)}{\gamma} \qquad \eta = \int_0^\infty G(t)dt \qquad J_e^0 = \frac{1}{\eta^2}\int_0^\infty tG(t)dt$$

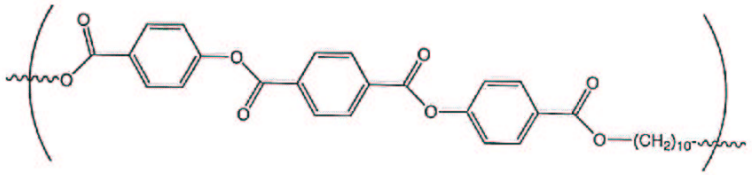
2. Oscillatory shear

$$G^*(\omega) = i\omega\int_0^\infty G(t)e^{i\omega t}dt = G'(\omega) + iG''(\omega) \qquad \eta = \lim_{\omega\to o}\frac{G''(\omega)}{\omega} \qquad J_e^0 = \frac{1}{\eta^2}\lim_{\omega\to 0}\frac{G'(\omega)}{\omega^2}$$

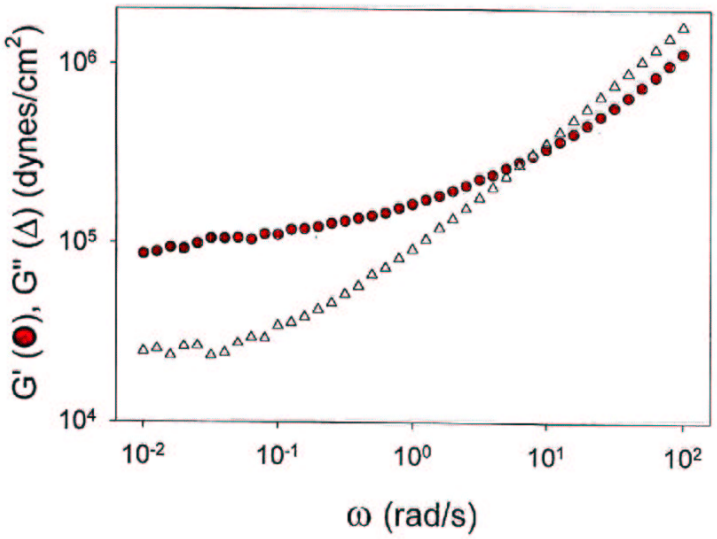


Rheological Response of Materials

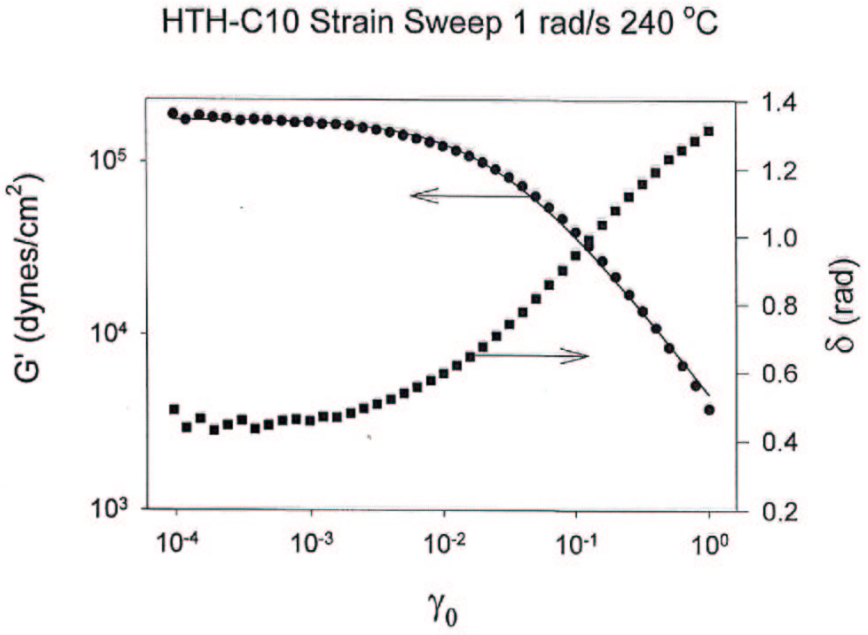




Main-Chain Smectic HTH-C10 240 °C



$\gamma_o = 0.005$

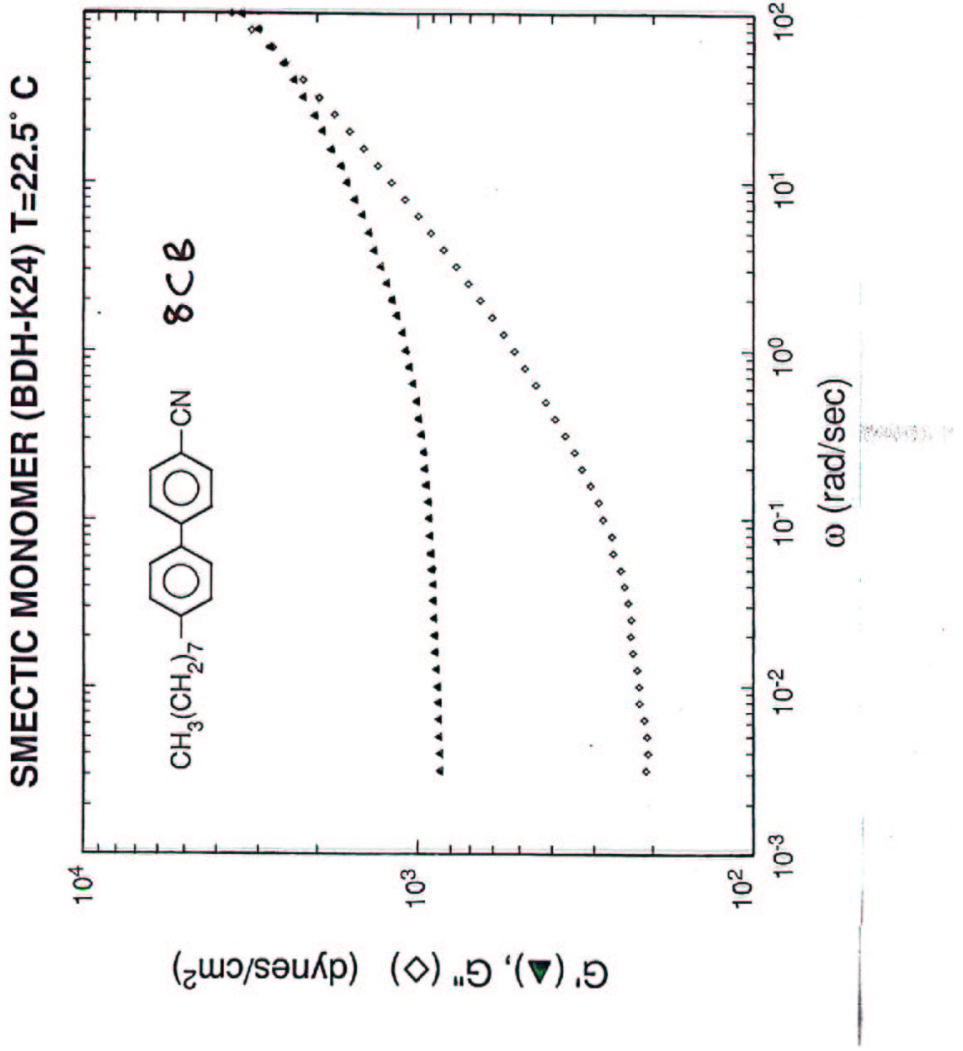


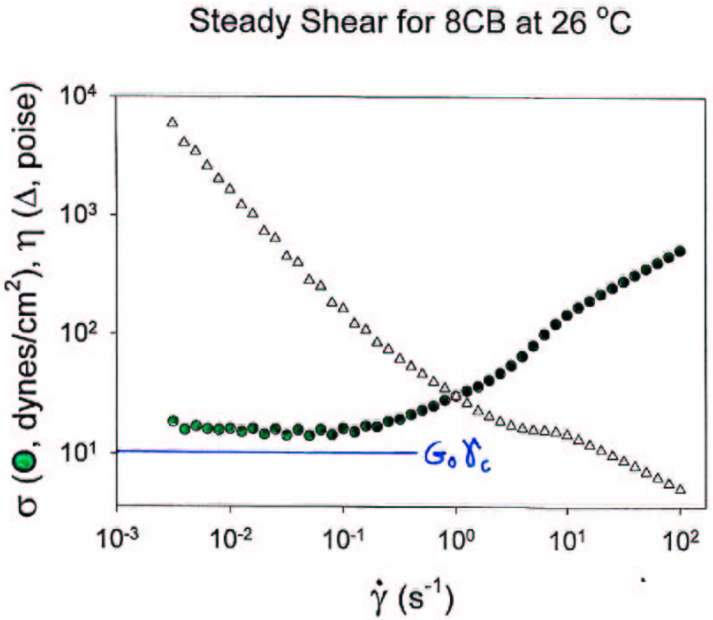
$$G'(\omega,\gamma_0) = \frac{G'(\omega,0)}{1+\gamma_0/\gamma_c}$$

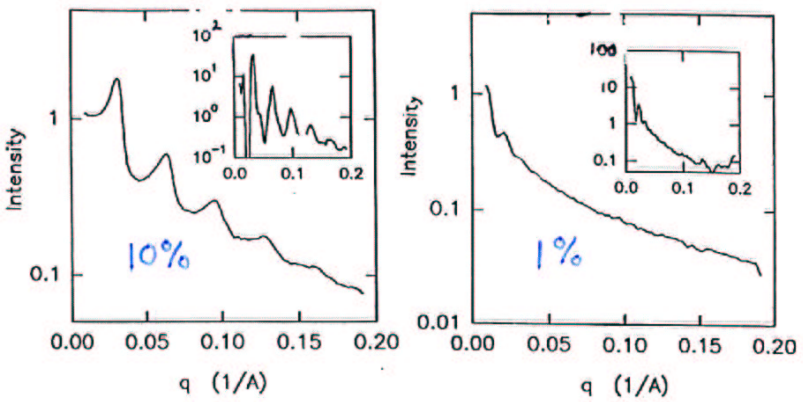
Applied Strain $\gamma(t) = \gamma_0 \sin\omega t$

Large Strain limit is constant stress

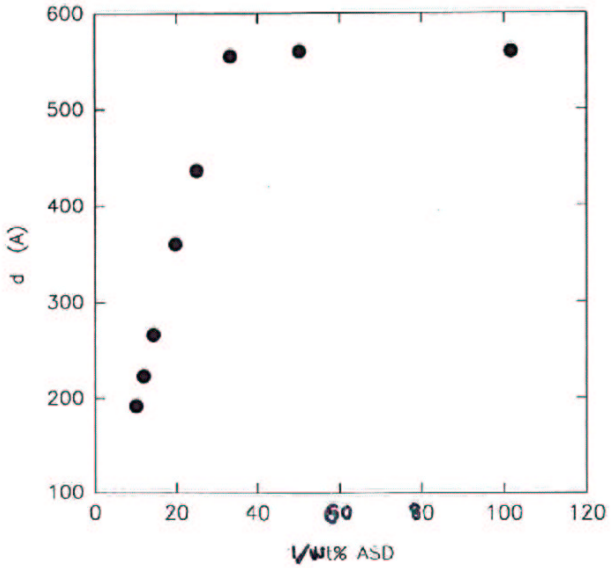
$$G'(\omega,\gamma_0)\,\gamma_0 = G'(\omega,0)\,\gamma_c$$

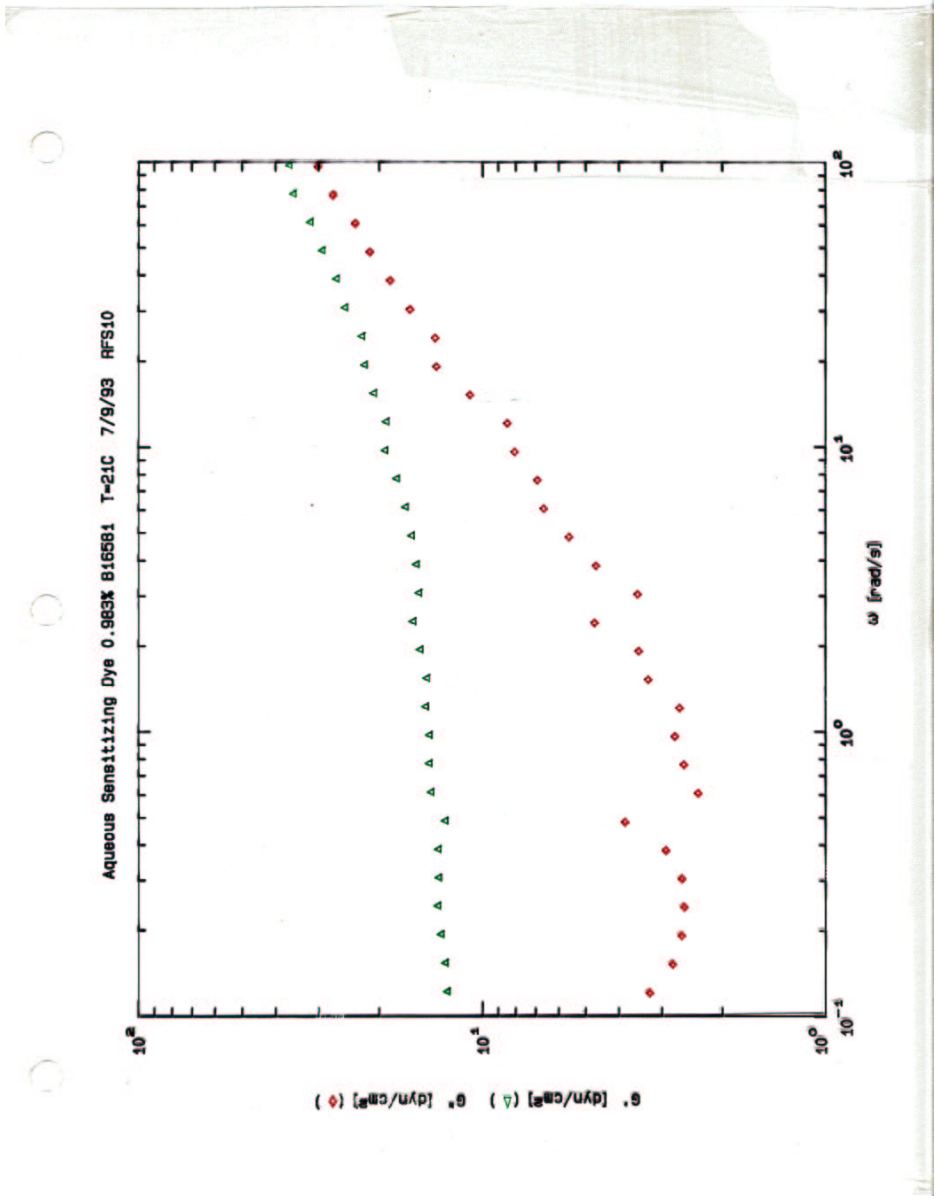


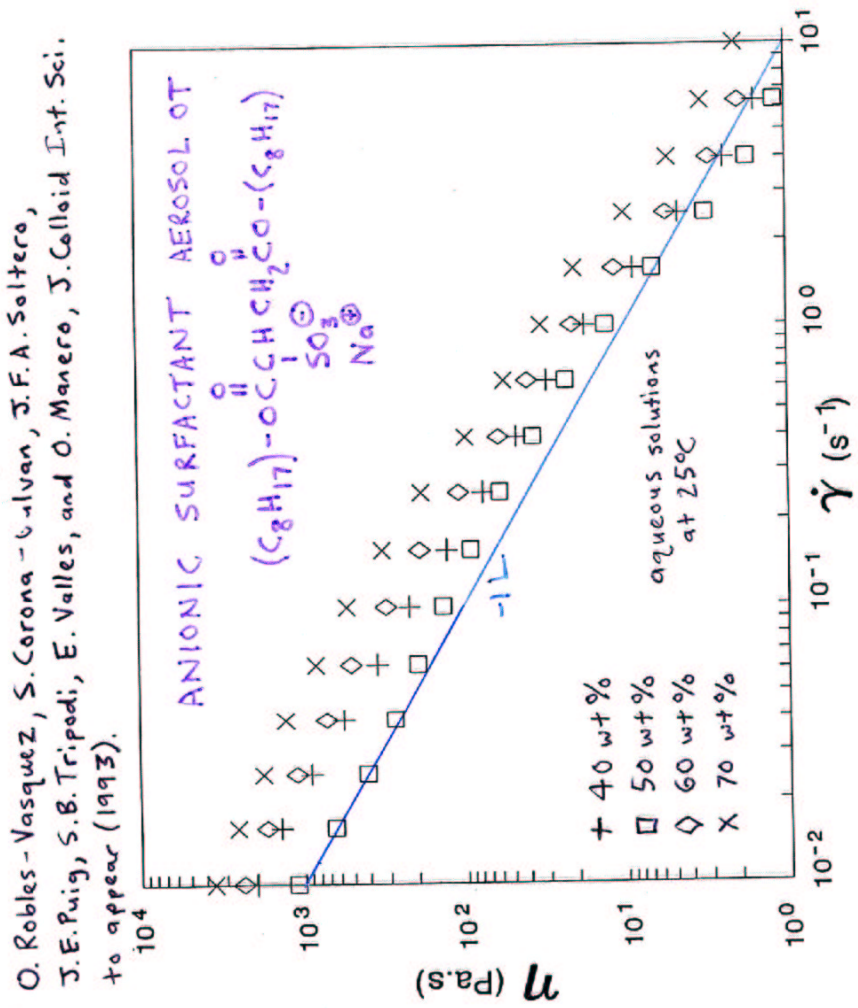




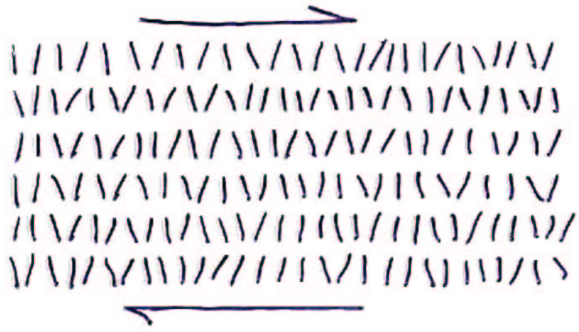
DYE SALTS IN WATER




Aqueous Sensitizing Dye 0.983X B16681 T=21C 7/9/93 RFS10
G' [dyn/cm²] (Δ) G" [dyn/cm²] (◇)
ω [rad/s]


O. Robles-Vasquez, S. Corona-Galvan, J.F.A. Soltero, J.E. Puig, S.B. Tripodi, E. Valles, and O. Manero, J. Colloid Int. Sci. to appear (1993).
ANIONIC SURFACTANT AEROSOL OT
(C8H17)-OCCHCH2CO-(C8H17)
SO3⊖ Na⊕
-1-
+ 40 wt%
□ 50 wt%
◇ 60 wt%
× 70 wt%
aqueous solutions at 25°C
η (Pa.s)
γ̇ (s⁻¹)

DEFECT-FREE SMECTICS IN PARALLEL ALIGNMENT ARE LIQUIDS

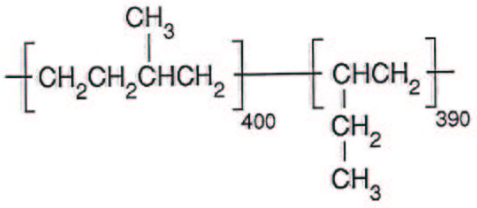


DEFECTS : DISCLINATIONS
DISLOCATIONS
FOCAL CONICS

DEFECTS MAKE THE MATERIAL A SOLID, EVEN IF THERE ARE ONLY A FEW DEFECTS PER LAYER.

THERMAL EQUILIBRIUM ⇒ FINITE POPULATION OF DEFECTS

PEP-PEE-2 DIBLOCK COPOLYMER (F.Bates)



M=50000
T_{OD} = 96° C

Symmetric ⇒ Lamellar

PEP M/M_e = 18 T_g = -56° C
PEE M/M_e = 2.5 T_g = -20° C

$$\chi = \frac{4.69}{T\,(K)} + 4.44 \times 10^{-4}$$

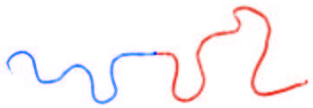
for PEP-PEE-2 at 30° C : χN = 12.6

Δ = interface width
d = lamellar spacing

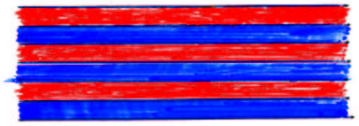
$$\frac{\Delta}{d} \cong (\chi N)^{-2/3} = 0.18 << 1 \Rightarrow \text{strong segregation}$$

$$\frac{d}{bN^{1/2}} \cong (\chi N)^{1/6} = 1.5 \therefore \text{weakly stretched}$$

DIBLOCK COPOLYMERS

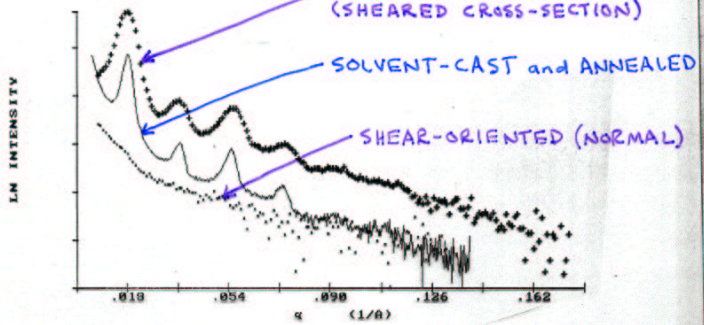


SHEAR-ORIENTED LAMELLAE

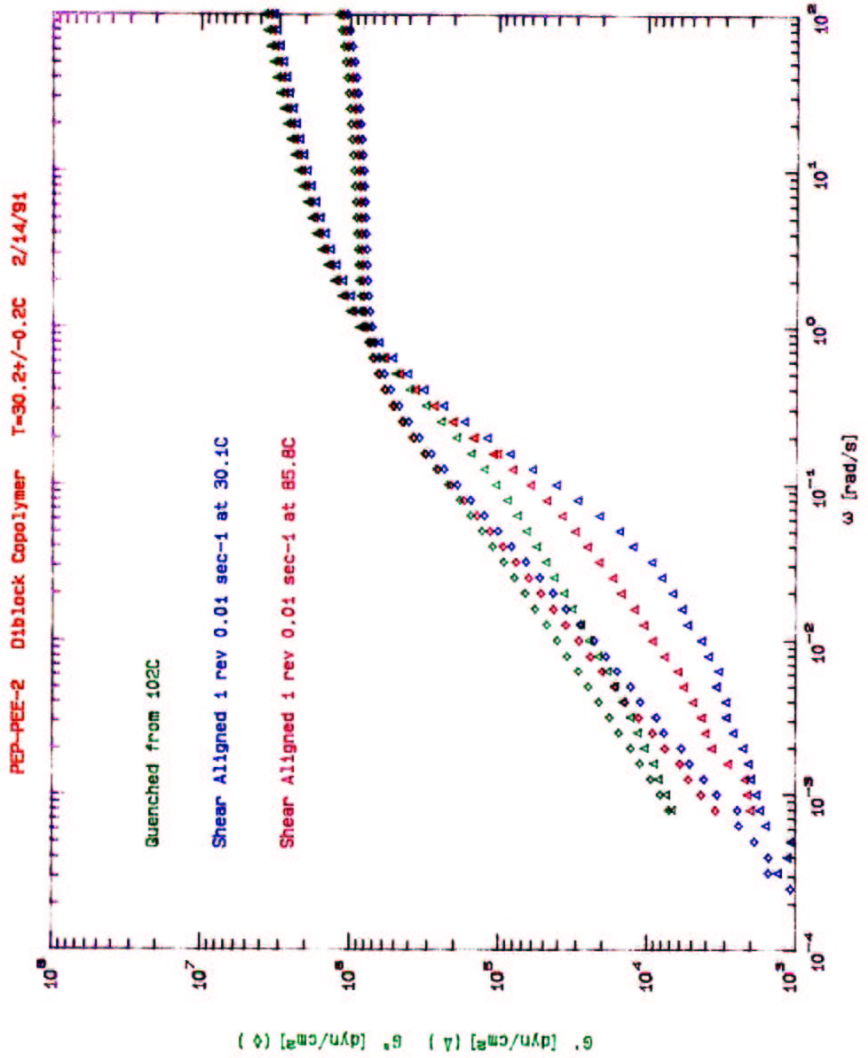


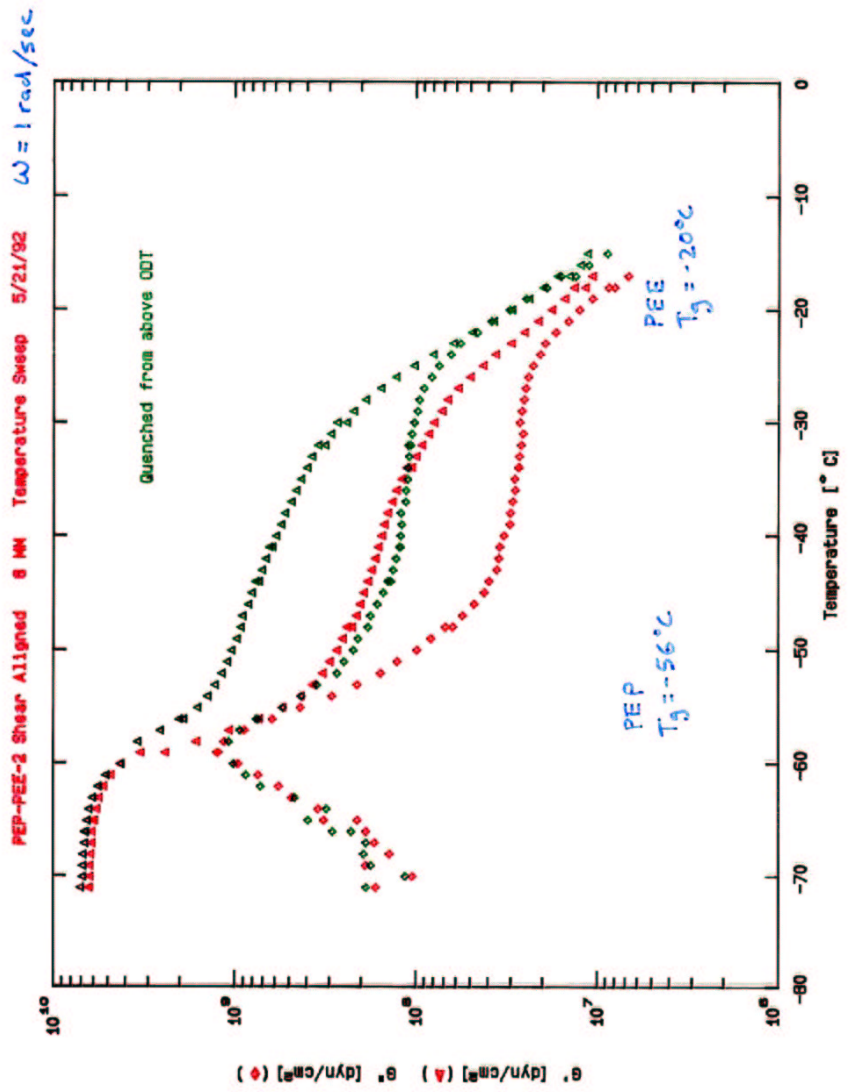
TORSION BETWEEN CIRCULAR FLAT PLATES
(PARALLEL PLATE GEOMETRY)

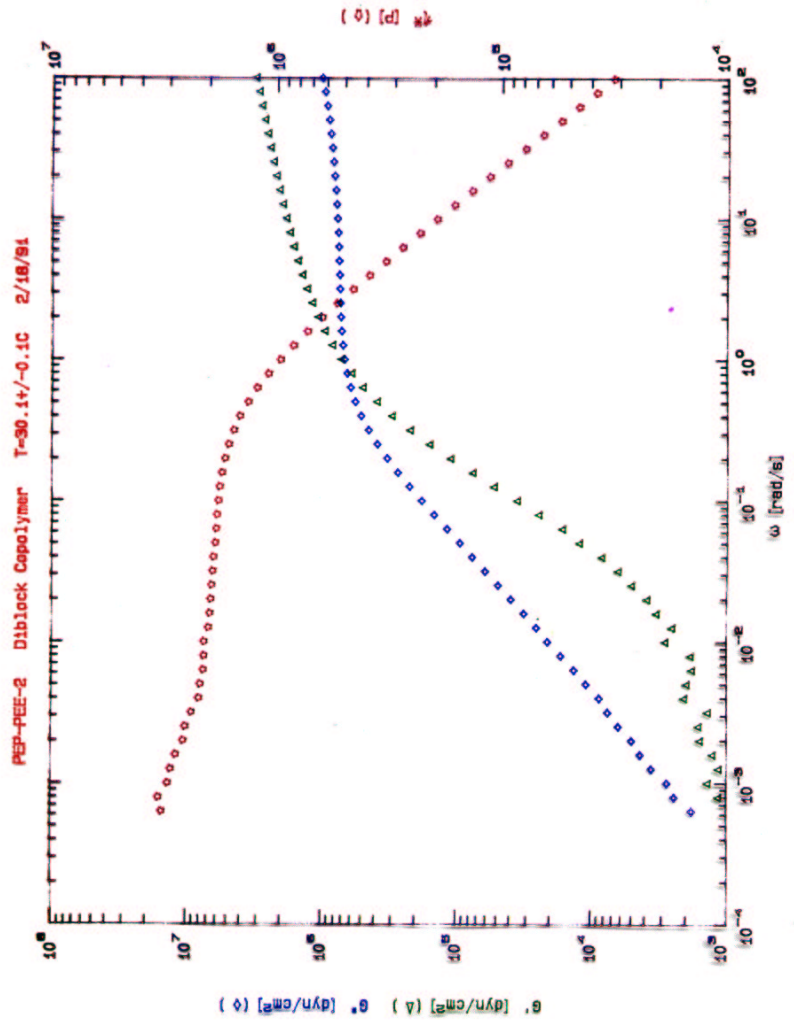
SAXS

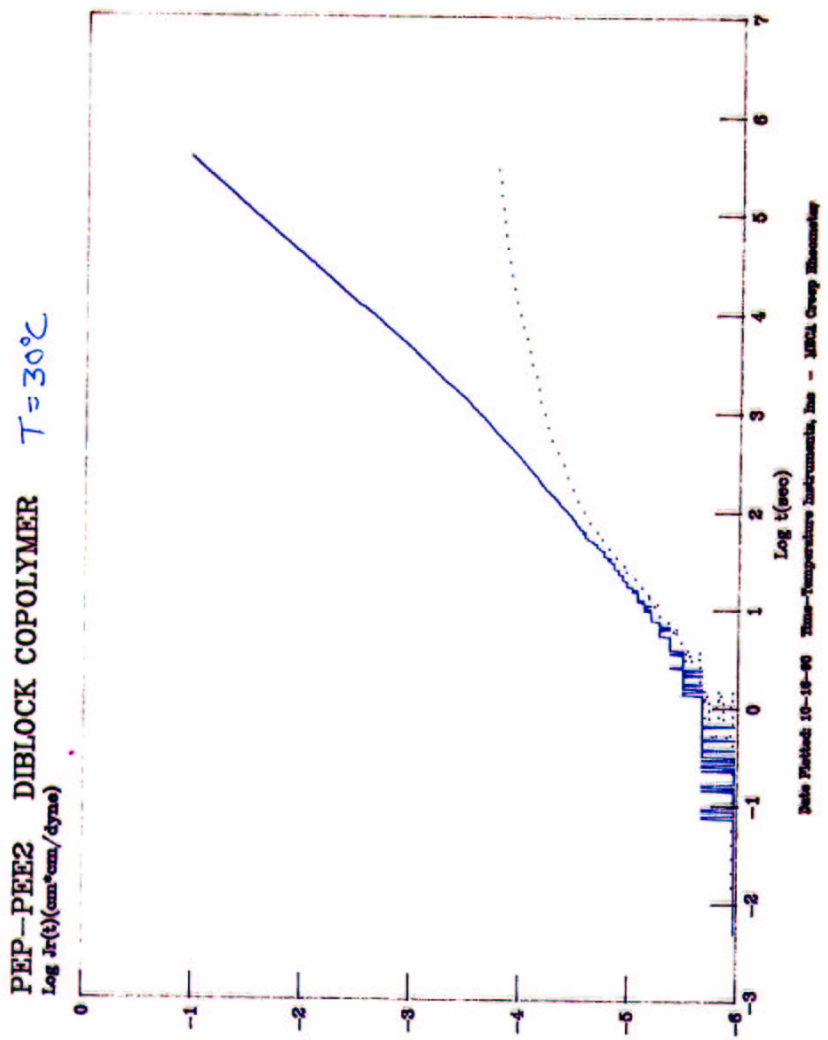


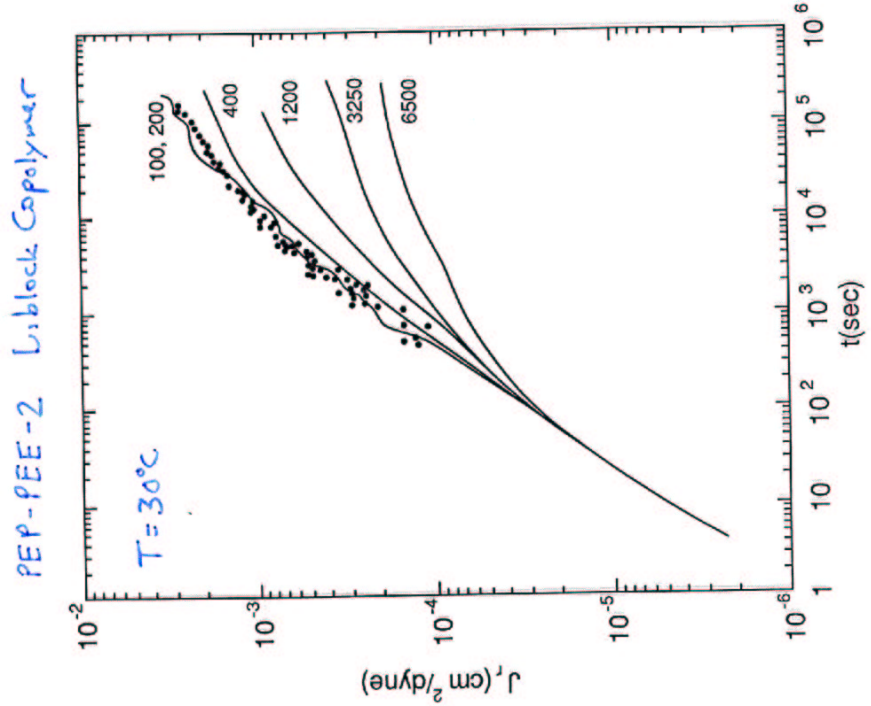
KRATKY CAMERA DATA OF M.R. LANDRY



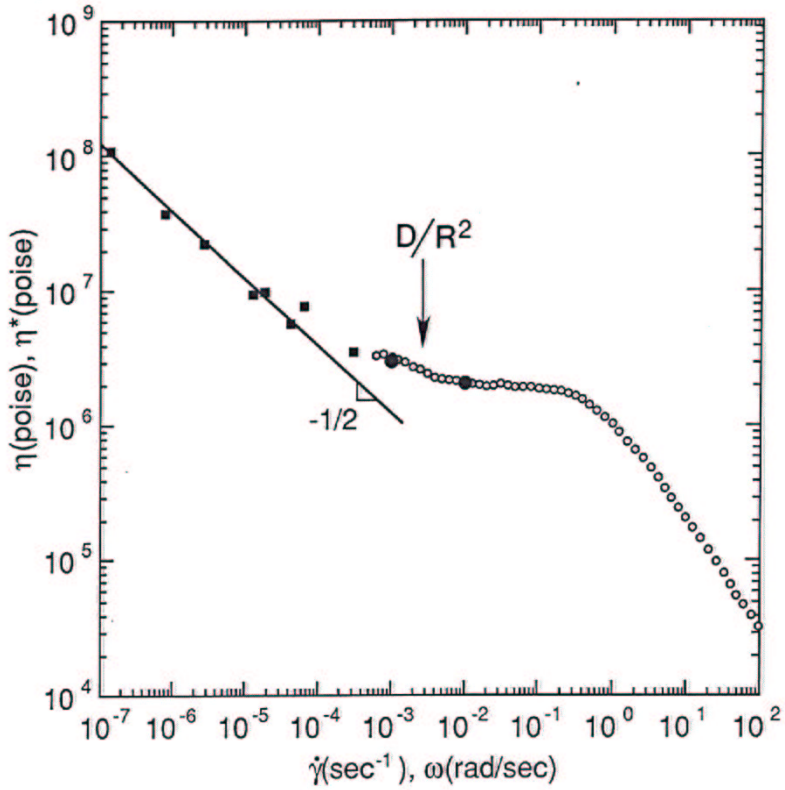

PEP-PEE-2 Shear Aligned 8 MM Temperature Sweep 5/21/92 ω = 1 rad/sec
Quenched from above ODT
PEE
Tg = -20°C
PEP
Tg = -56°C
Temperature [° C]
G' [dyn/cm²] (Δ) G" [dyn/cm²] (◇)


PEP-PEE-2 Diblock Copolymer T=30.1+/-0.1C 2/18/91
ω [rad/s]
G' [dyn/cm²] (Δ) G" [dyn/cm²] (◇)

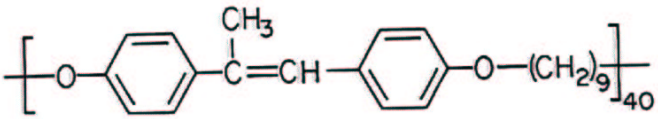

PEP–PEE2 DIBLOCK COPOLYMER
T=30°C
Log Jr(t)(cm²/dyne)
Log t(sec)

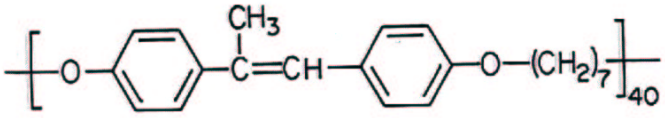

PEP-PEE-2 Liblock Copolymer
T=30°C
100, 200
400
1200
3250
6500
J_r (cm²/dyne)
t(sec)

PEP-PEE-2 LAMELLAR DIBLOCK COPOLYMER T = 30°C



MAIN-CHAIN LC POLYMER



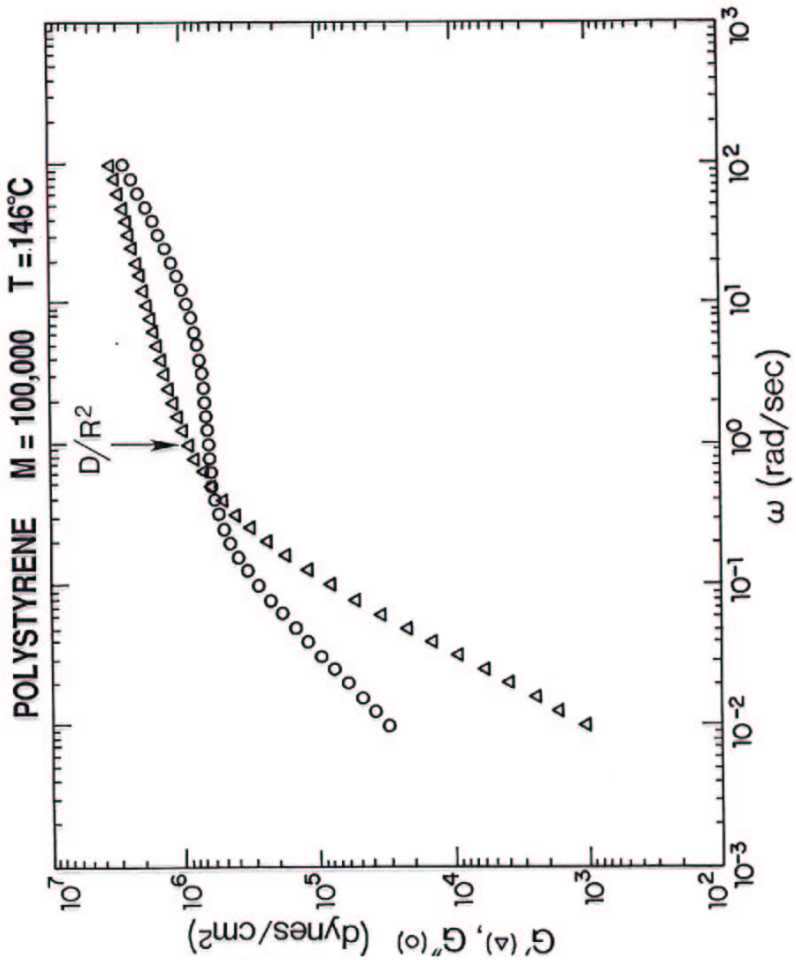


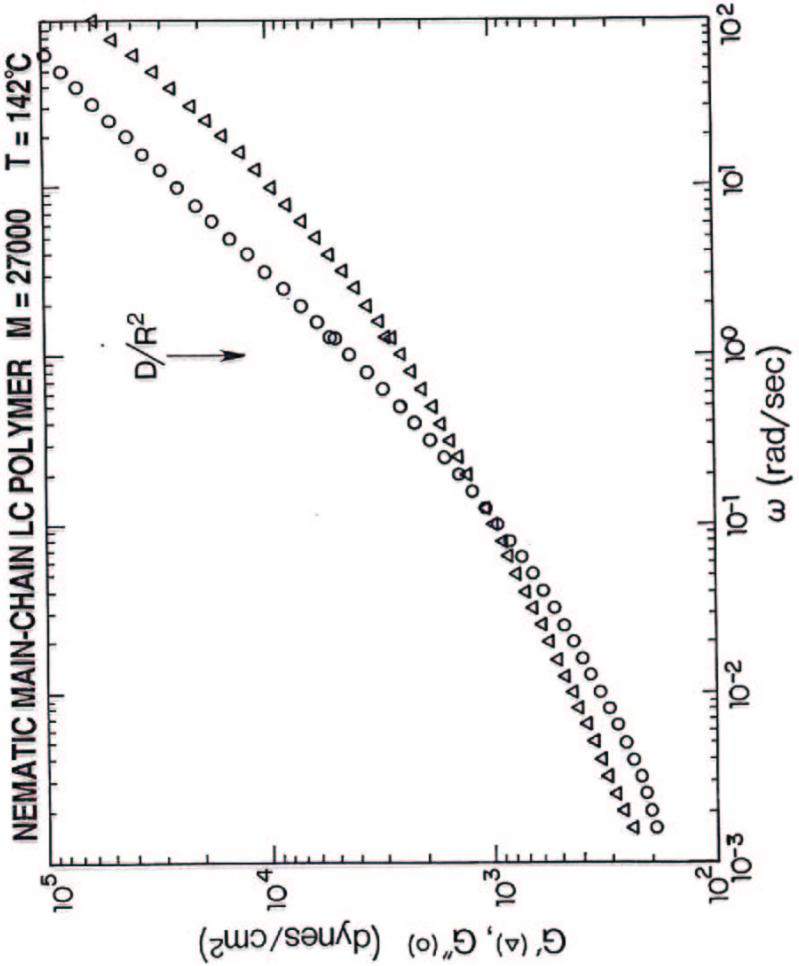
Random Copolymer ⇒ Wide Nematic Temperature Range

Polyether ⇒ No Interchange Reactions

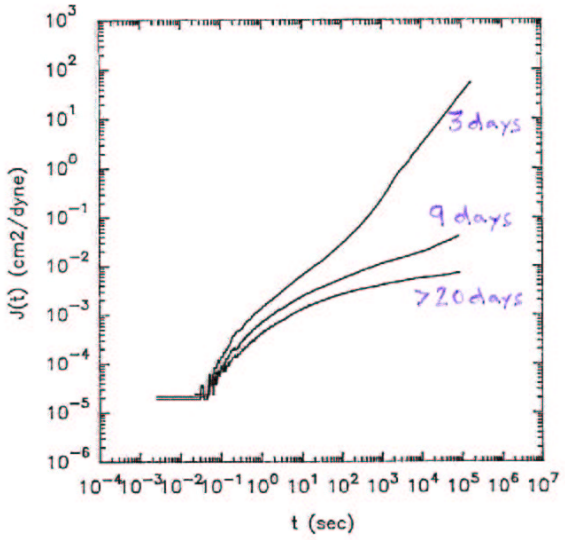
M_w = 27000

T_g = 21°C
T_M = 95°C
T_x = 127°C
T_{NI} = 200°C

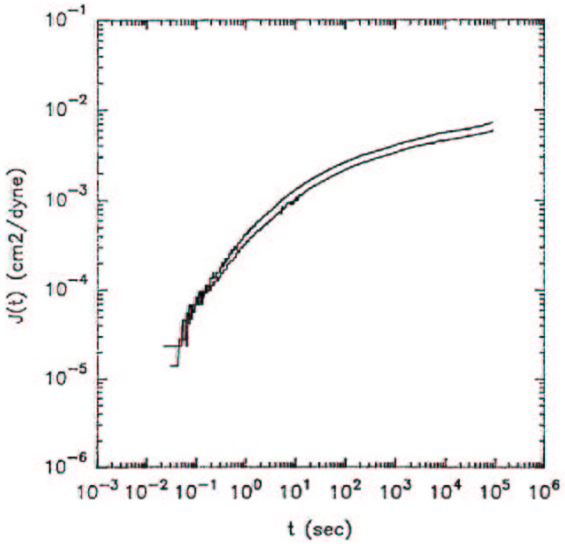

POLYSTYRENE M = 100,000 T = 146°C
D/R²
G′ (Δ), G″ (○) (dynes/cm²)
ω (rad/sec)


NEMATIC MAIN-CHAIN LC POLYMER M = 27000 T = 142°C
D/R²
G′ (Δ), G″ (○) (dynes/cm²)
ω (rad/sec)

Creep on DHMS-7,9 σ = 37 dynes/cm^2
Nematic Main Chain LC Polymer T = 150°C



Creep and Recovery in Final State T = 150°C
Main Chain Nematic LC Polymer 37 dynes/cm^2



What is the origin of the modulus?

MODULUS VALUES

Smectic Polymer G = 30000 dynes/cm^2
Smectic Monomer G = 1000 dynes/cm^2
Nematic Polymer G = 100 dynes/cm^2

Nematic Monomer? G = 3 dynes/cm^2 ?

Is the modulus controlled by the defect spacing?

G = kT/L^3 G = K/L^2

This suggests the nematic polymer has L = 800 Å.

Defect Motion in Structured Fluids

Orowan Equation:

$$\dot{\gamma} \approx \rho b \bar{v} \approx \rho b \mu \sigma \sim \frac{b \mu \sigma}{\xi^2}$$

$\dot{\gamma}$ shear rate

ξ dislocation spacing

$\rho \sim 1/\xi^2$ dislocation line density

b Burgers vector

$\bar{v}$ average dislocation velocity

σ shear stress

$\mu \equiv \bar{v}/\sigma$ mobility

E. Orowan, Proc. Phys. Soc. (London) 52, 8 (1940).

Orowan Equation in Smectic (or Lamellar) Phases

$$\dot{\gamma} \approx \rho b \bar{v} \sim \frac{b\mu\sigma}{\xi^2}$$

For smectics:

$$\sigma \sim G \approx \frac{kT}{\xi^3}$$

Combine them:

$$\dot{\gamma} \sim \sigma^{5/3}$$

derived by M. Kléman, Rheol. Acta 39, 223 (1999)

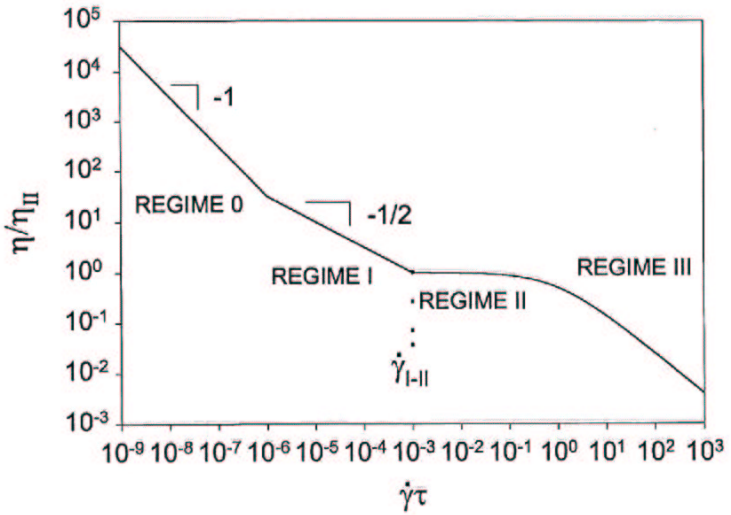
Viscosity:

$$\eta \equiv \frac{\sigma}{\dot{\gamma}} \sim \sigma^{-2/3} \sim \dot{\gamma}^{-2/5}$$

Defect Spacing:

$$\xi \sim \sigma^{-1/3} \sim \dot{\gamma}^{-1/5}$$

Four Regimes for Viscosity of Nematic Liquid Crystals



Orowan Equation in Nematic Phases

$$\dot{\gamma} \approx \rho b \bar{v} \sim \frac{b\mu\sigma}{\xi^2}$$

For nematics:

$$\sigma \sim G \approx \frac{K}{\xi^2}$$

Combine them:

$$\dot{\gamma} \sim \sigma^2$$

Viscosity:

$$\eta \equiv \frac{\sigma}{\dot{\gamma}} \sim \sigma^{-1} \sim \dot{\gamma}^{-1/2}$$

Defect Spacing:

$$\xi \sim \sigma^{-1/2} \sim \dot{\gamma}^{-1/4}$$

Rheology of region I flow in a lyotropic liquid-crystal polymer: The effects of defect texture

Lynn Walker and Norman Wagner[a)]

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

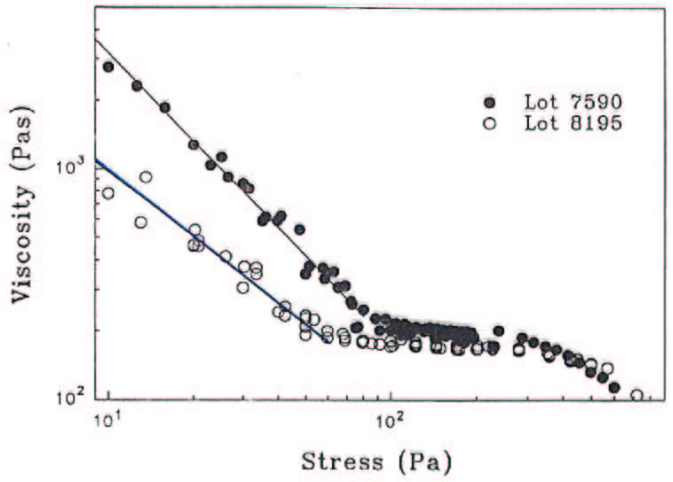


FIG. 4. Steady-state flow curves of 60 wt % HPC-E in water solutions prepared from two different polymer lots. The power-law slopes (stress vs shear rate) in region I are 0.49 (lot 8195) and 0.44 (lot 7590). Although region I is shifted the main aspects of the flow curves are insensitive to changes in polymer characteristics.

$\eta \sim \sigma^{-1} \sim \dot{\gamma}^{-1/2}$ predicted by Marrucci (1984)

based on different physics

Rheology of region I flow in a lyotropic liquid-crystal polymer: The effects of defect texture

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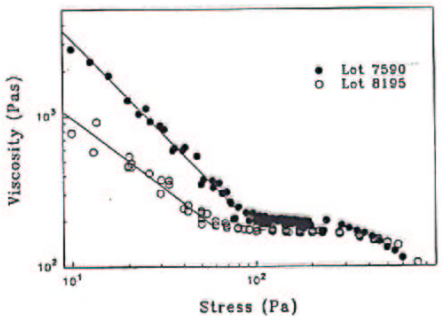
Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

J. Rheol. 38(5), September/October 1994



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Rheol Acta 34:137–146 (1995)

ORIGINAL CONTRIBUTION

Stefano Guido
Nino Grizzuti

Phase separation effects in the rheology of aqueous solutions of hydroxypropylcellulose

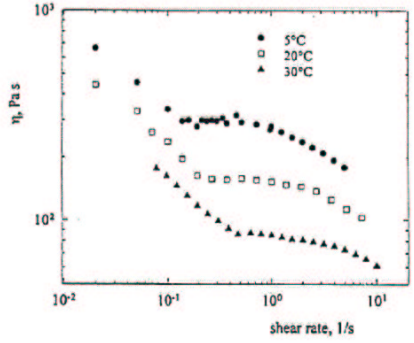


Fig. 1 Viscosity vs. shear rate for the HPC-E 60% wt solution at various temperatures

Macromolecules **1997**, *30*, 508–514

In Situ Analysis of the Defect Texture in Liquid Crystal Polymer Solutions under Shear

Lynn M. Walker,† William A. Kernick III, and Norman J. Wagner*

Colburn Laboratory, Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

Received April 19, 1996; Revised Manuscript Received August 15, 1996[⊗]

ABSTRACT: A combination of two *in situ* small-angle scattering techniques are employed to compare the texture and molecular order in flowing LCPs that exhibit constant viscosities (region II) and shear thinning (region I) at low shear rates. The microstructure is characterized by an overall molecular orientation S_{eff}, a texture correlation length a_c, and an aspect ratio a_r. Results indicate that in region I the texture has a high density of defects and a low overall molecular order, with shear primarily acting to distort the texture. In region II the texture is distorted in the shear direction and the overall molecular orientation is higher, while the primary influence of shear is to refine texture size. The critical Ericksen stress balance is also tested experimentally.

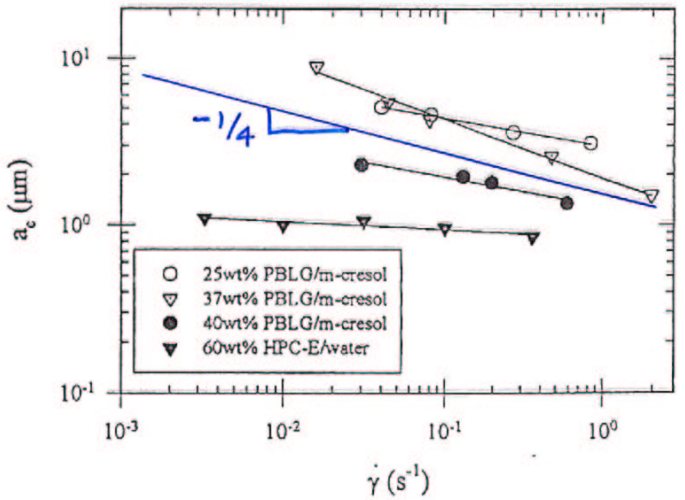


Figure 7. Correlation lengths a_c determined from F-SALS patterns for solutions that exhibit region I (filled) at low shear rates and those that exhibit only region II (open) at low shear rates.

$\xi \sim \dot{\gamma}^{-1/2}$ predicted by Burghardt + Fuller (1990)

$\xi \approx \left(\frac{K}{\sigma}\right)^{1/2} \sim \dot{\gamma}^{-1/4}$ predicted by Larson + Doi (1991)

Macromol. Chem. Phys. 199, 471–483 (1998)

Feature Article

Molecular orientation and rheology in sheared lyotropic liquid crystalline polymers

Wesley R. Burghardt
Department of Chemical Engineering, Northwestern University, Evanston, IL 60208, USA:

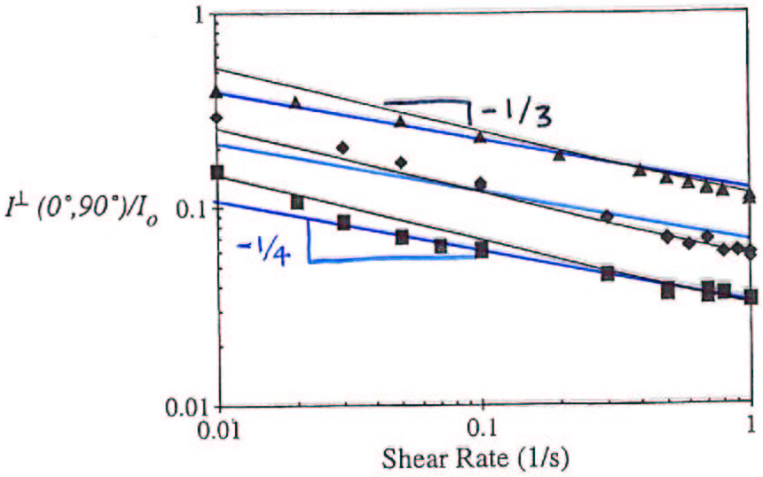
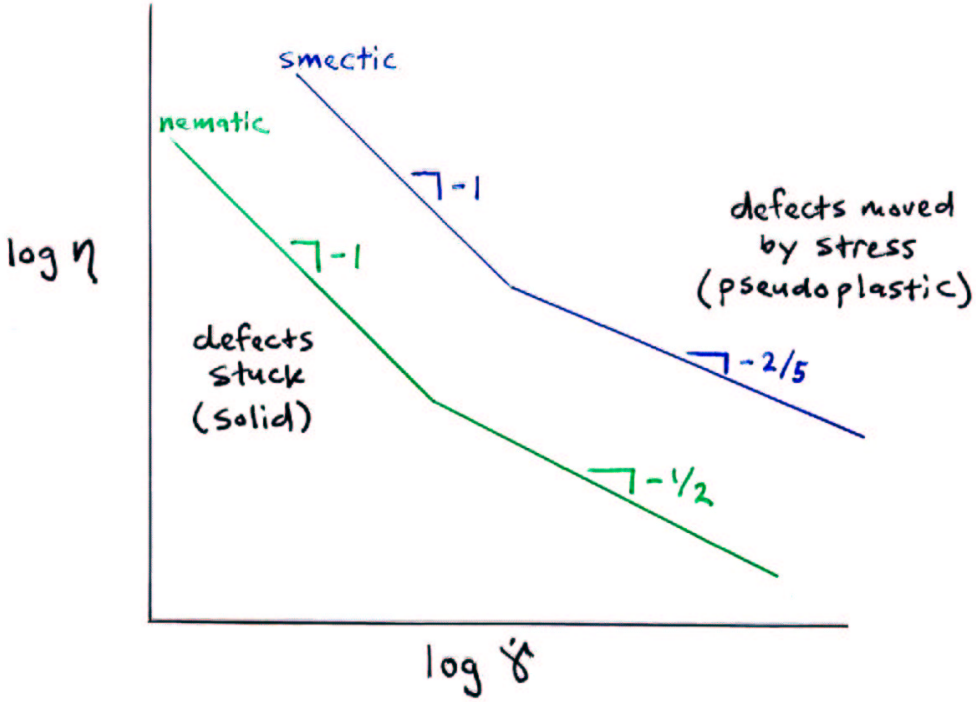


Fig. 6. Light intensity measured between crossed polarizers oriented perpendicular and parallel to the flow direction, as a function of steady shear rate for a 13.5 wt.-% solution of PBDG (M = 298 000) in m-cresol. Lines are drawn according to the formula $C\dot{\gamma}^{-0.33}$, with values of C proportional to the sample thicknesses used: 1.94 mm (▲), 0.94 mm (♦) and 0.54 mm (■)

$$I^{\perp} \sim \frac{\dot{\gamma} t}{\lambda^2}$$

$$\dot{\gamma} = \rho b \bar{v} \sim \frac{\sigma}{\dot{\gamma}^2}$$



Conclusions

Any material with **long range order** has a **defect texture** that makes it a viscoelastic **solid**.

- Thermotropic Smectic Monomers
- Lyotropic Lamellar Phases
- Smectic Polymers
- Lamellar Block Copolymers?
- Nematic Polymers
- Thermotropic Nematic Monomers?