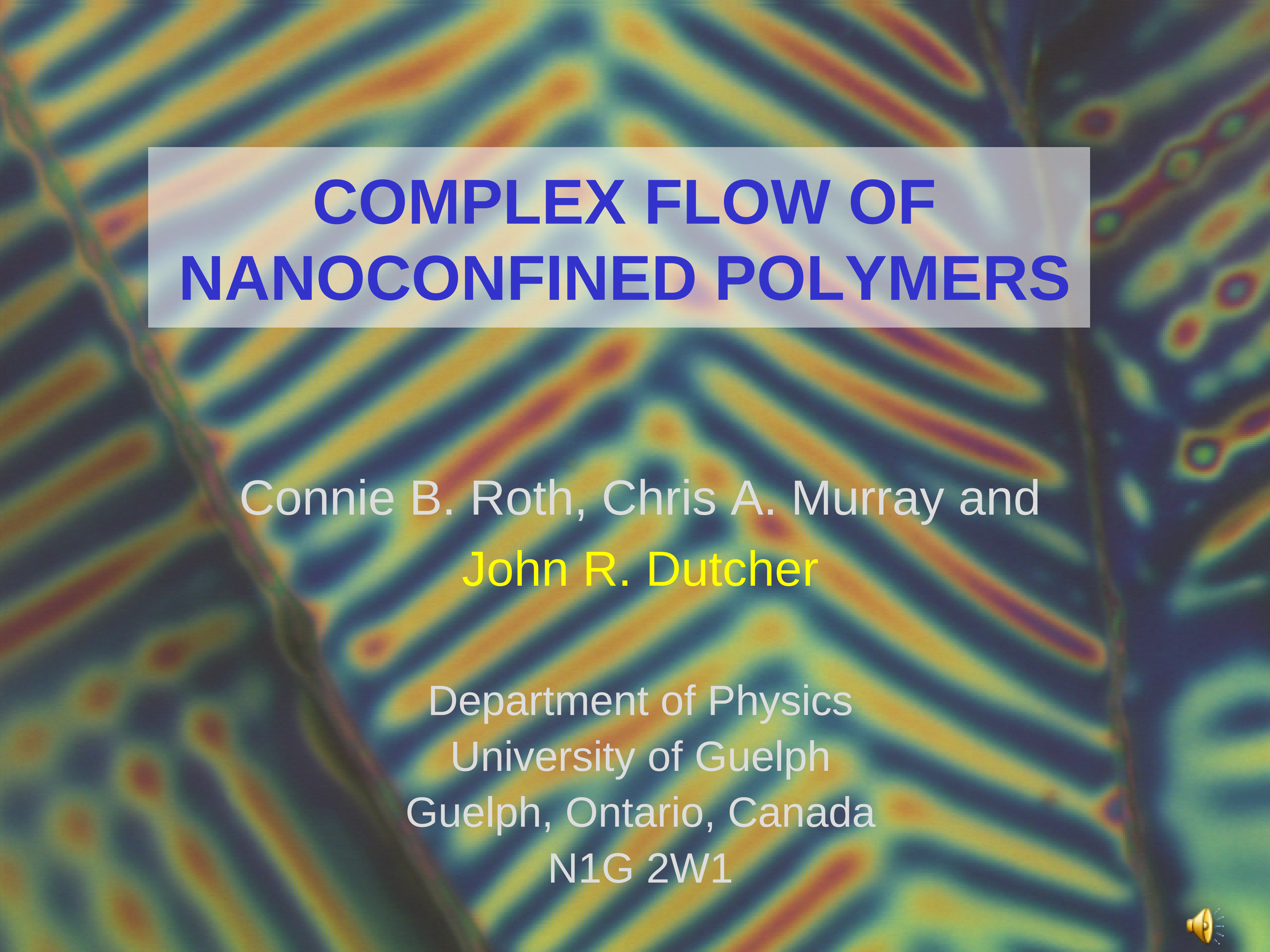
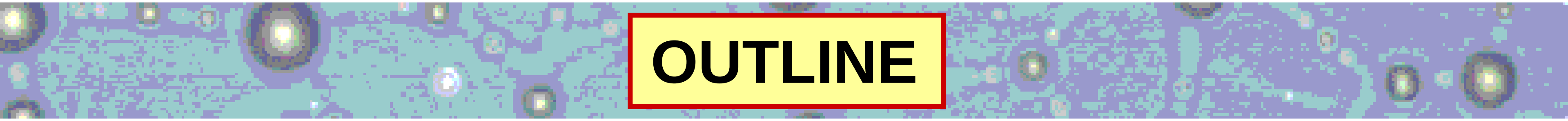


COMPLEX FLOW OF NANOCONFINED POLYMERS

Connie B. Roth, Chris A. Murray and
John R. Dutcher

Department of Physics
University of Guelph
Guelph, Ontario, Canada
N1G 2W1



OUTLINE

- instabilities in freely-standing liquid films

- hole growth in freely-standing PS films
  - ideal geometry for probing complex flow
    - shear thinning
    - convective constraint release relaxation mechanism
  - hole growth occurs for T comparable to T_g^{bulk}

- hole growth in freely-standing PS/PI/PS trilayer films
  - holes in central PI layer

- summary & conclusions

CURRENT PROJECTS

POLYMERS

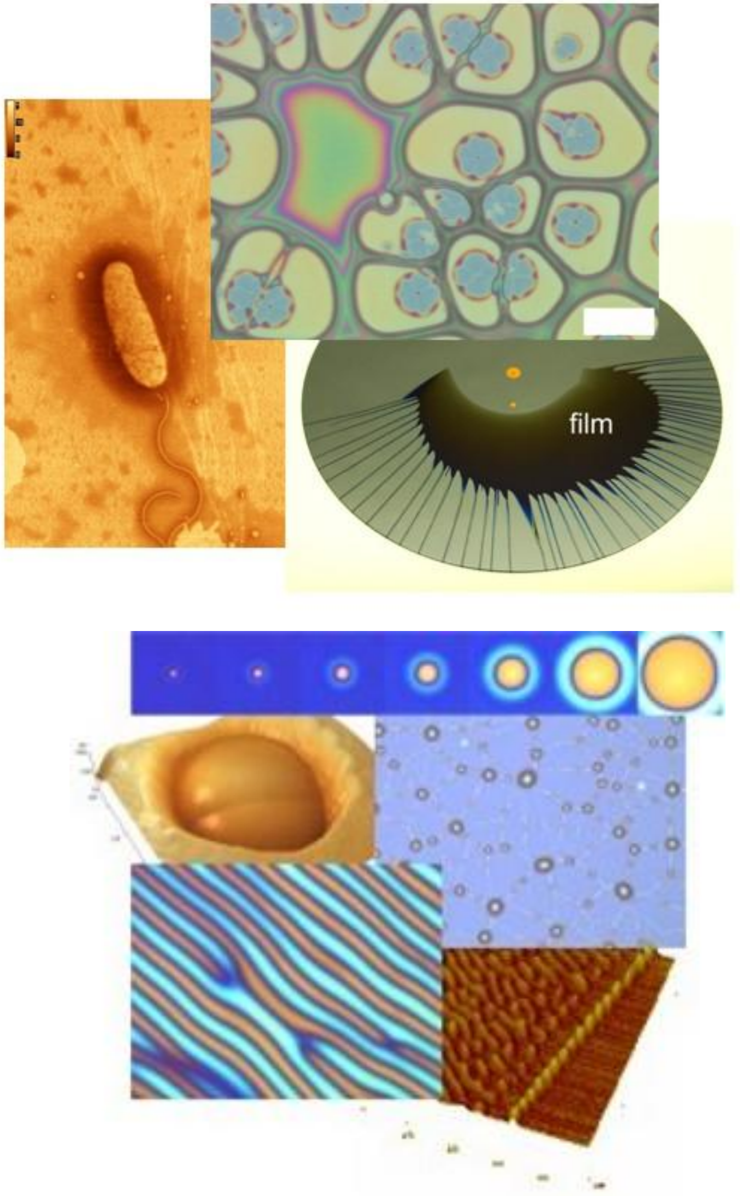
- molecular mobility
  - glass transition & hole growth
- instabilities & pattern formation
- biodegradable polymers

BIOPOLYMERS

- polypeptides & proteins – lipid membranes & polymer brushes

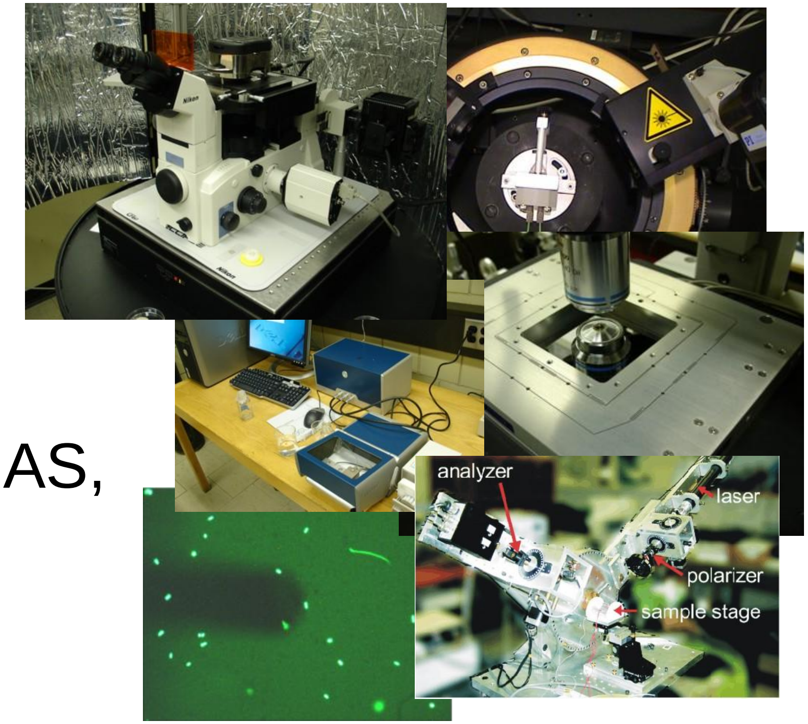
BACTERIAL CELLS

- bacterial adhesion & physical properties of bacteria & biofilms



SURFACE-SENSITIVE PROBES

- to measure structure, dynamics, interaction forces, molecular conformations, adsorption kinetics, we use
  - atomic force microscopy
  - ellipsometry
  - surface plasmon resonance
  - quartz crystal microbalance
  - optical tweezers
  - TIRF
  - infrared techniques (PM-IRRAS, ATR-FTIR)
  - surface circular dichroism
  - TEM
  - differential pressure techniques



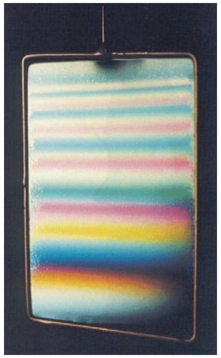
THIN LIQUID FILMS

- thin liquid films occur in everyday life
  - adhesives (superglue)
  - lubricants (on cornea of eye, engine piston)
  - spray coatings (paint, herbicides, fibers)
  - printing (ink on transparency or tape)
  - soap bubbles & films
  - foams (shaving cream, cappuccino)

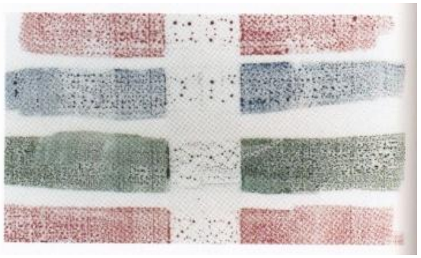
stability desirable/ essential

  - water films (water spotting, hydroplaning)

stability undesirable

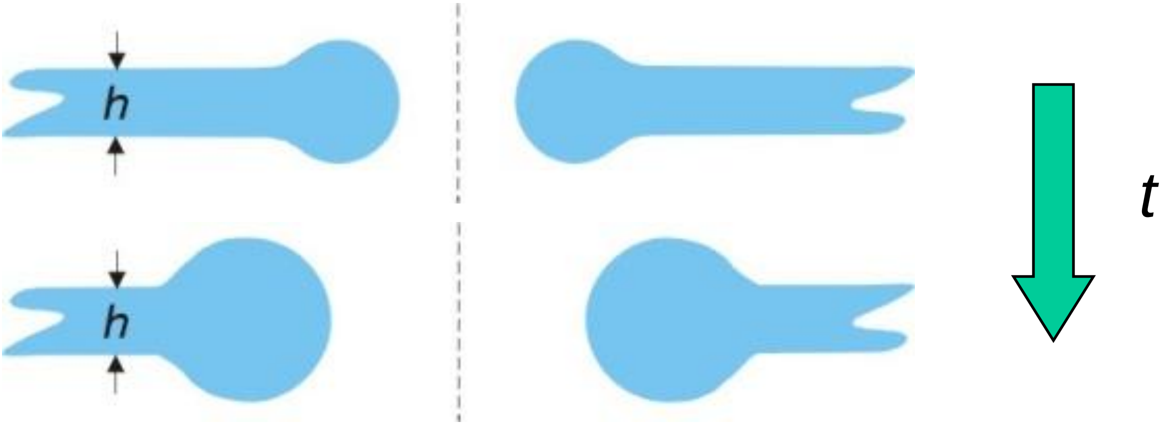




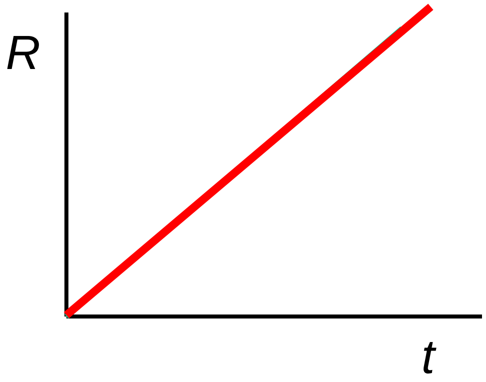


HOLE GROWTH IN NON-VISCOUS FILMS

- – fluid collects in a rim
- – rest of film undisturbed



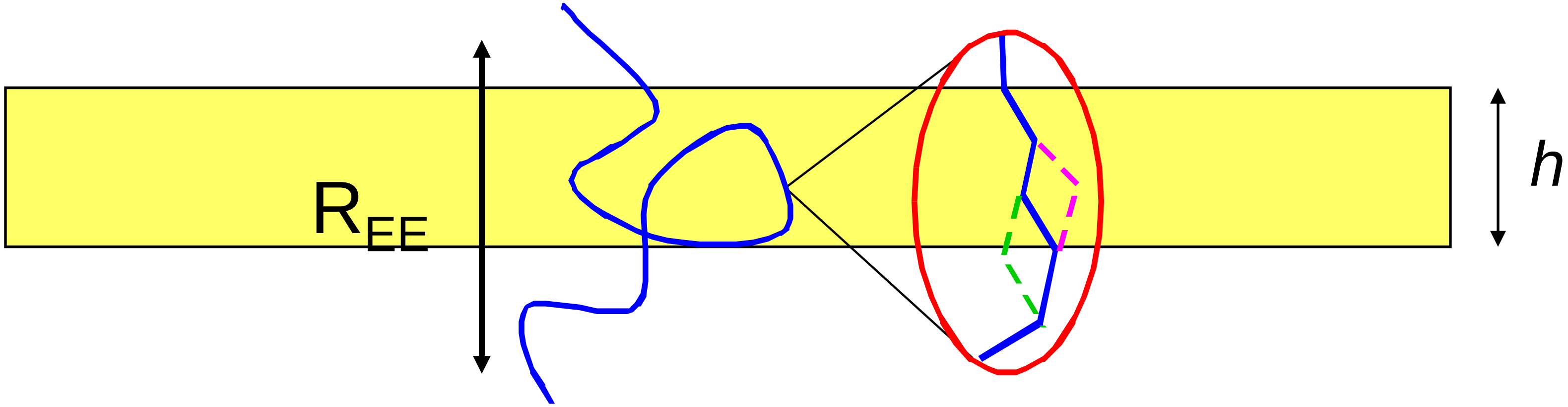
- hole radius grows linearly with time



[Taylor, Proc. Roy. Soc. (1959)]
[Culick, J. Appl. Phys. (1960)]

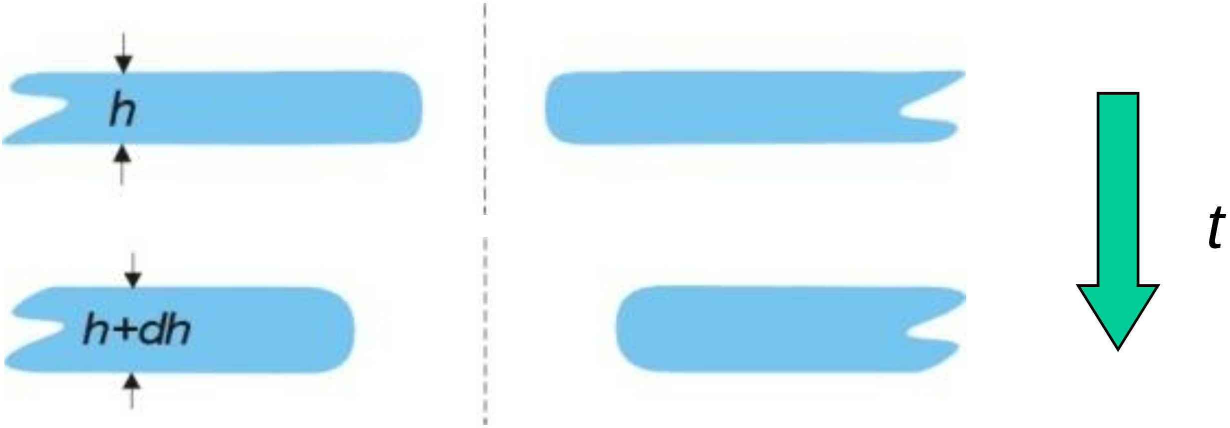
POLYMER MOLECULES

- polymers are complex molecules
  - – different length scales ranging from segment size to overall chain size $R_{EE} \sim M_w^{0.5}$
  - – different time scales ranging from segmental relaxation to diffusion of entire molecules



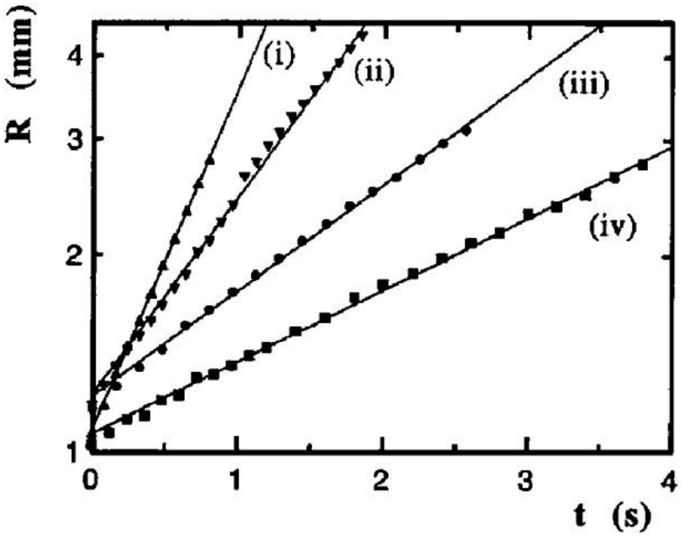
  - – effect of confinement in thin films
    - – changes in conformation & dynamics

HOLE GROWTH IN VISCOUS FILMS



- no rim
- film thickens uniformly

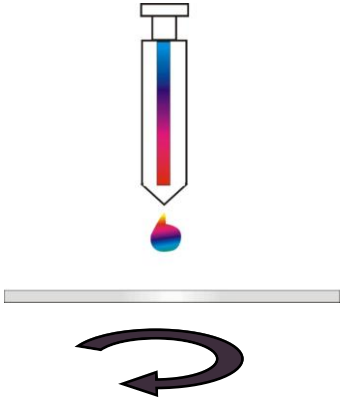
- hole radius grows exponentially with time



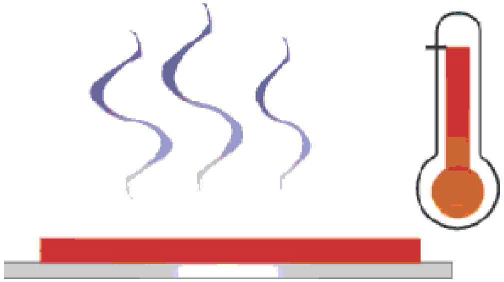
[Debrégeas *et al*., PRL (1995)]

FREELY-STANDING FILM PREPARATION

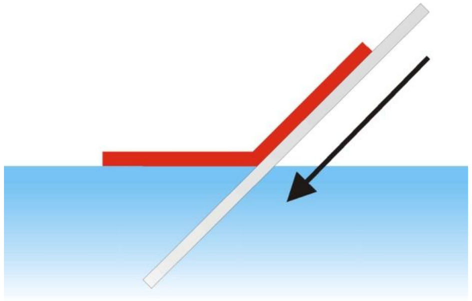
- high molecular weight, monodisperse polymers dissolved in good solvents



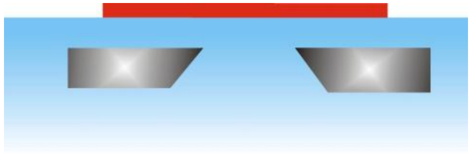
spincoat polymer
solution onto
mica substrate



anneal film
under vacuum



transfer film
onto water
surface



capture film
on holder
containing 4 mm
diameter hole

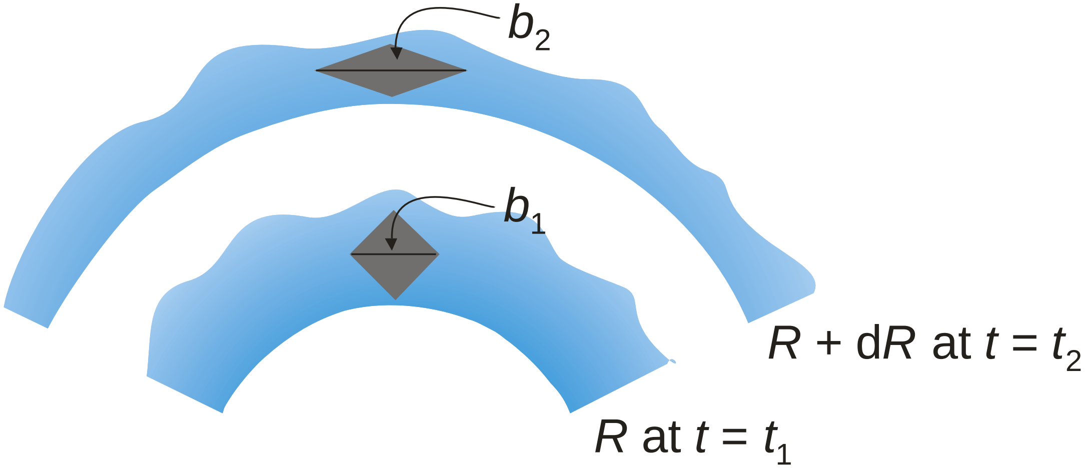
HOLE GROWTH IN POLYMER FILMS

– plug flow

– driven by surface tension

$\sigma = \dfrac{2\varepsilon}{h}$ at edge of hole; $\sigma \sim \dfrac{1}{r^2}$ into rest of film

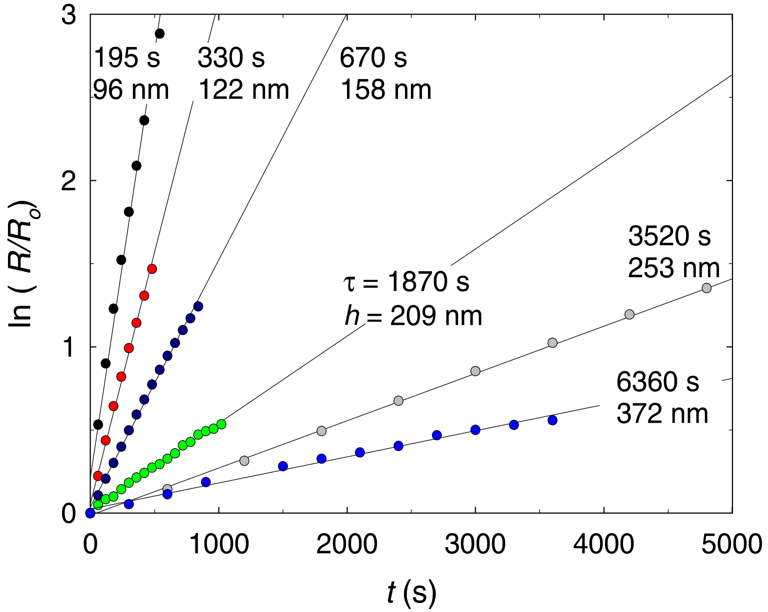
– polymer chains become aligned near edge of hole

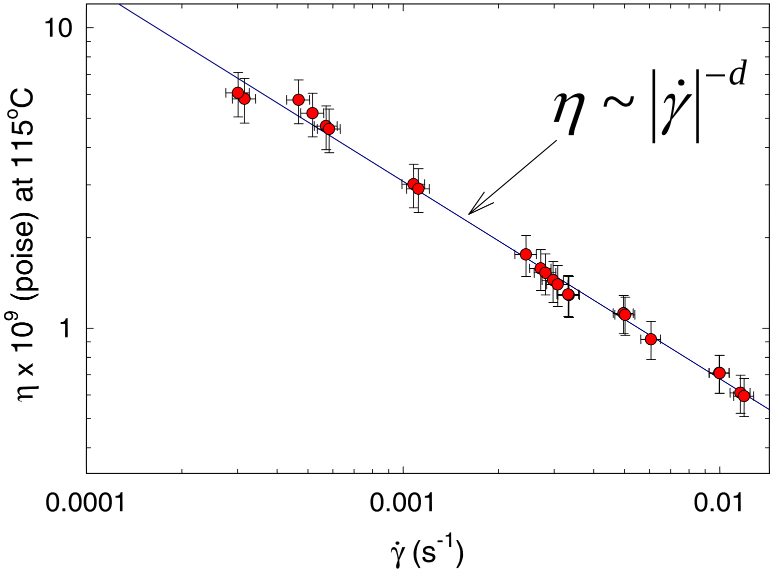


10 μm

PREVIOUS HOLE GROWTH IN PS FILMS

- optical microscopy of freely-standing polystyrene films
  - M_w = 717k
  - 96 nm < h < 372 nm
  - T = 115°C (T_g^{bulk} = 97°C)
  - exponential hole growth
  - decrease in viscosity for increasing strain rate
  - consistent with shear thinning

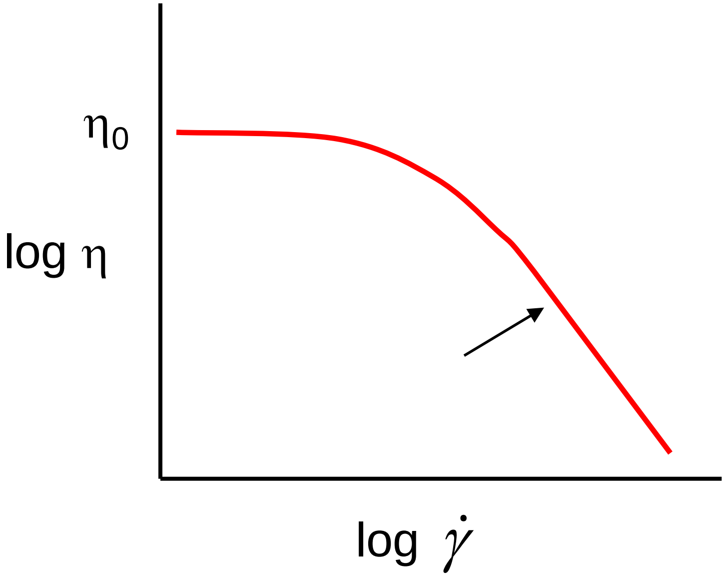


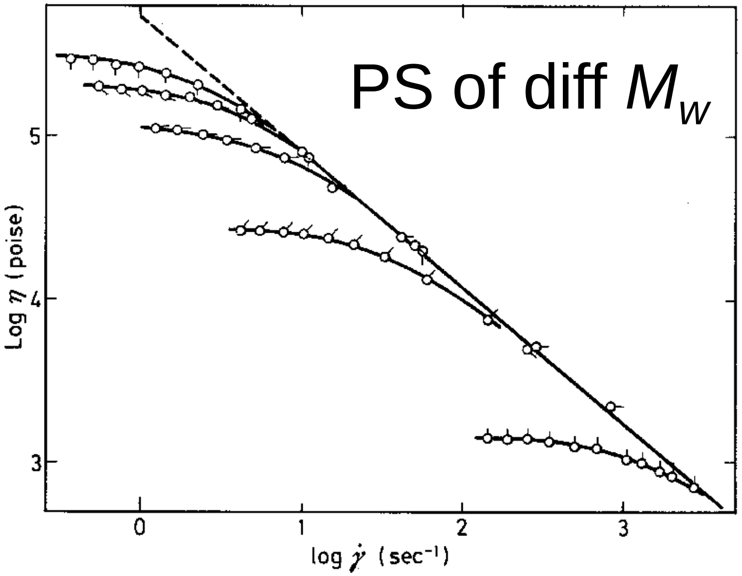


[Dalnoki-Veress *et al.*, PRE **59**, 2153 (1999)]

SHEAR THINNING OF POLYMERS

- decrease in viscosity η with increasing shear strain rate $\dot{\gamma}$





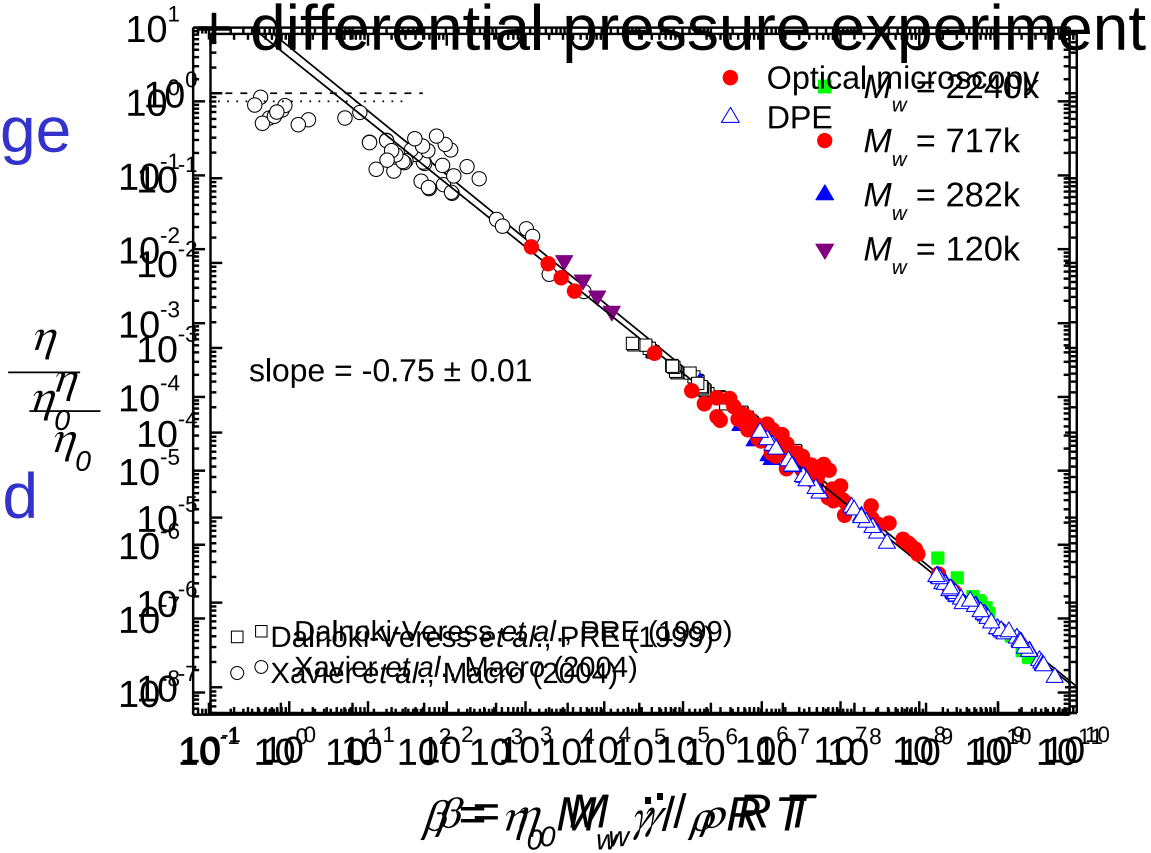
  - shear thinning only observed for entangled polymers
    [Peterlin, Adv. Macromol. Chem. **1**, 225 (1968)]
  - η is M_w-independent in nonlinear regime
    [Stratton, J. Colloid Interf. Sci. **22**, 517 (1966)]

SHEAR THINNING IN FREELY-STANDING PS FILMS

- different *T*, M_w and *h*
- use growth time τ to obtain viscosity η at edge of hole
- plot η/η_0 versus reduced shear strain rate β
- results consistent with viscous flow in presence of shear thinning

optical microscopy

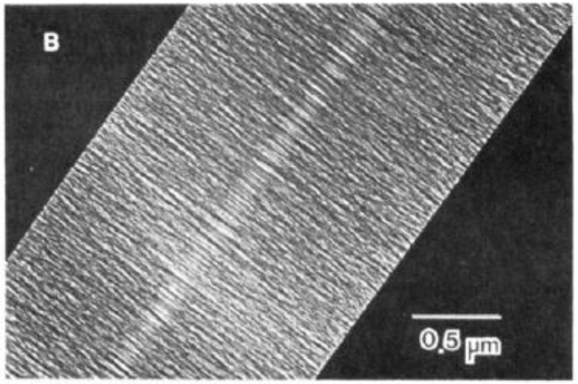
+ differential pressure experiment



[Roth & Dutcher, PRE **72**, 021803 (2005)]

FLOW AT SUCH LOW TEMPERATURES?

- in bulk, viscosity $\eta_0 \sim 10^{12}$ Pa•s at $T \sim T_g$
  - – expect both viscous and elastic effects important
  - – late stage hole growth is well-described by viscous flow

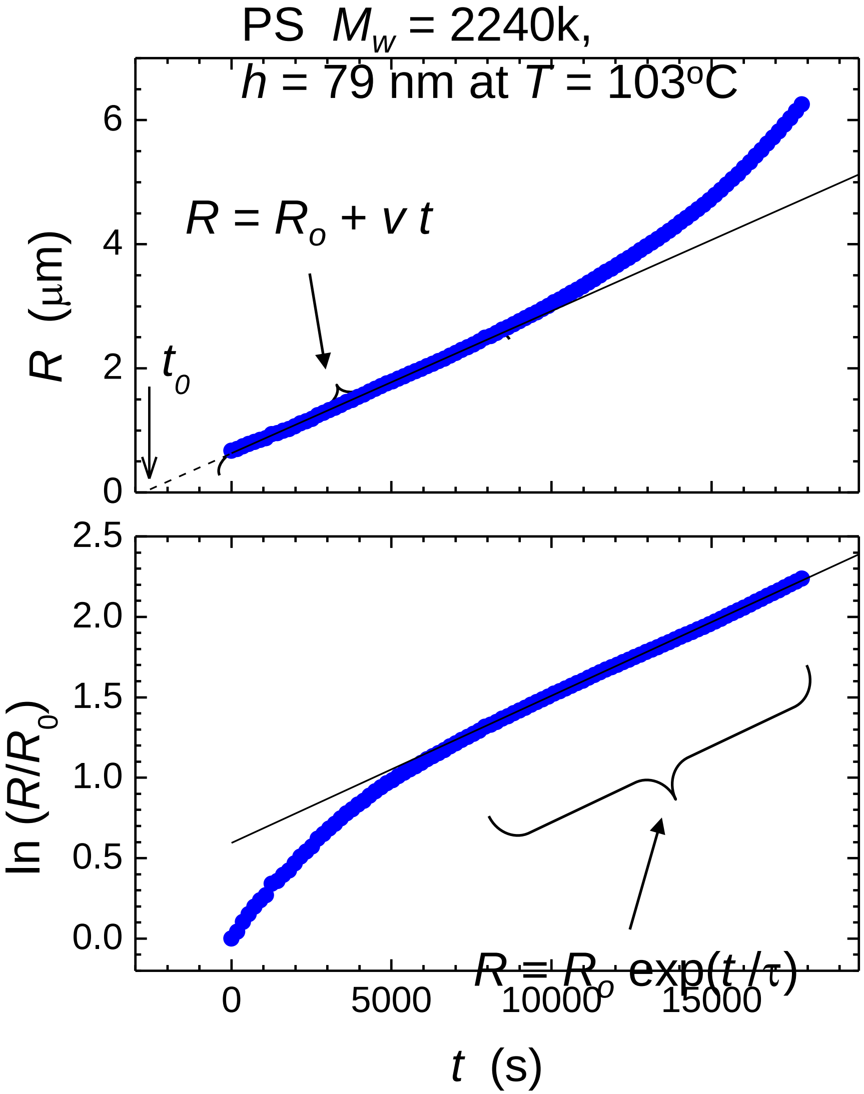


- previous studies of crazing of PS films [Berger & Kramer, Macro (1987)]
  - – chain scission at low temperatures
  - – chain disentanglement at strain rates & higher temps
    - – for M_w = 1800k: $T > 70^{o}$C for $\dot{\gamma} = 4.1 \times 10^{-6}$ s^{-1}
      $T > 90^{o}$C for $\dot{\gamma} \sim 10^{-2}$ s^{-1}
- comparable strain rates & temps for hole growth
  1.5×10^{-4} s$^{-1} < \dot{\gamma} < 2 \times 10^{-2}$ s^{-1} for 101^{o}C $< T < 117^{o}$C

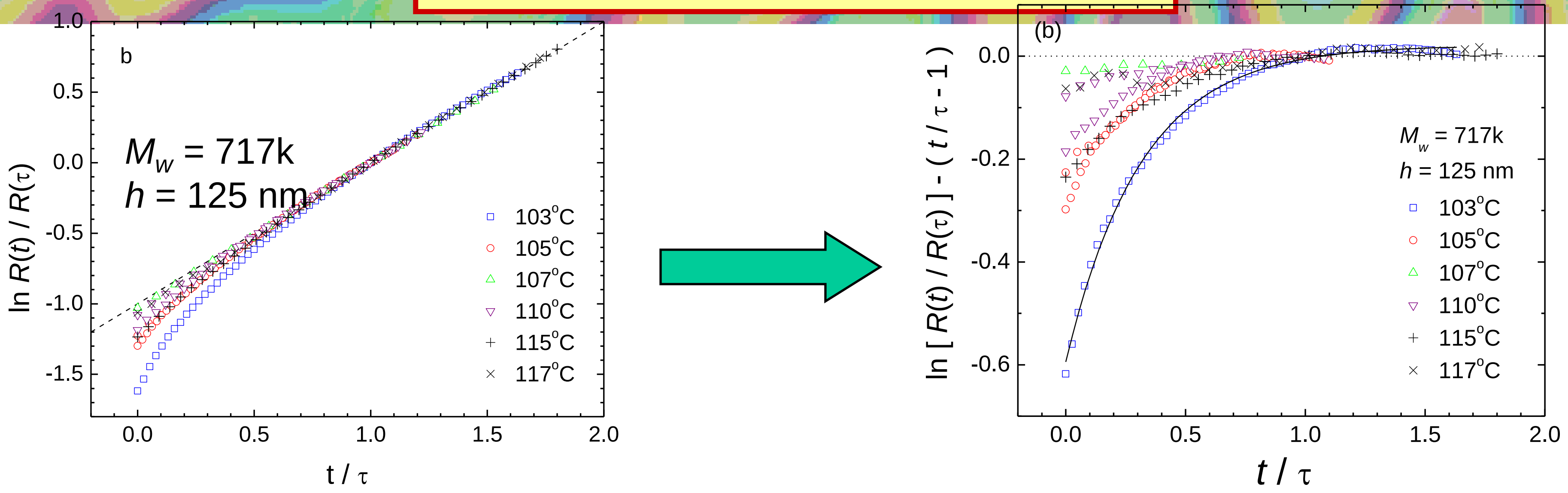
TRANSITION IN HOLE GROWTH

- measure $R(t)$ for single hole using optical microscopy
  - linear growth at early times
    - velocity v
  - exponential growth at late times
    - growth time τ
  - range of times for linear growth decreases with
    - increasing T
    - decreasing M_w

[Roth *et al*., PRE **72**, 021802 (2005)]



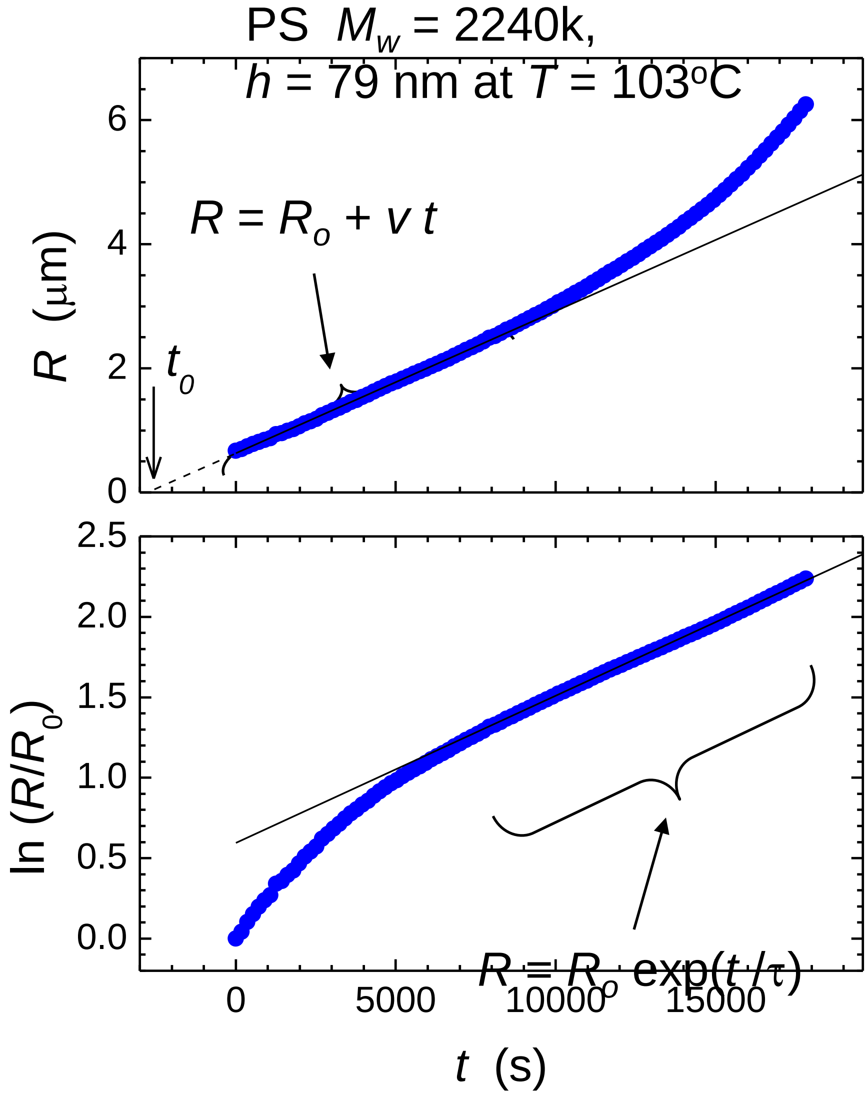
TRANSIENT BEHAVIOR



- scale axes: ln[$R(t)/R(\tau)$] vs t/τ
  - □ data sets coincide for t > τ
- isolate transient
  - – single exponential decay time τ_1

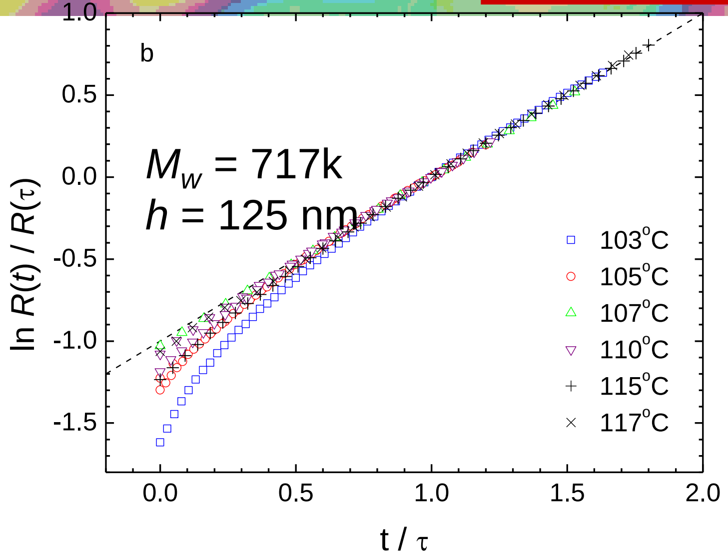
TRANSITION IN HOLE GROWTH

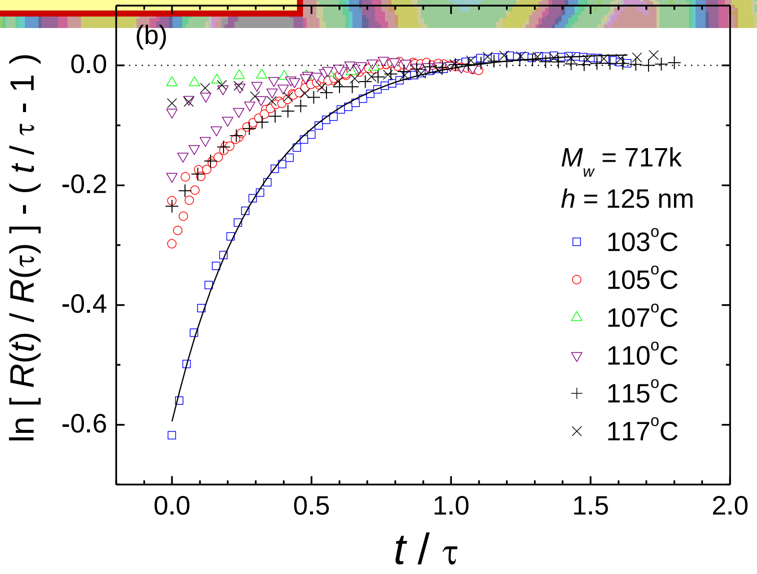
- measure *R*(*t*) for single hole using optical microscopy
  - linear growth at early times
    - velocity *v*
  - exponential growth at late times
    - growth time τ
  - range of times for linear growth decreases with
    - increasing *T*
    - decreasing M_w

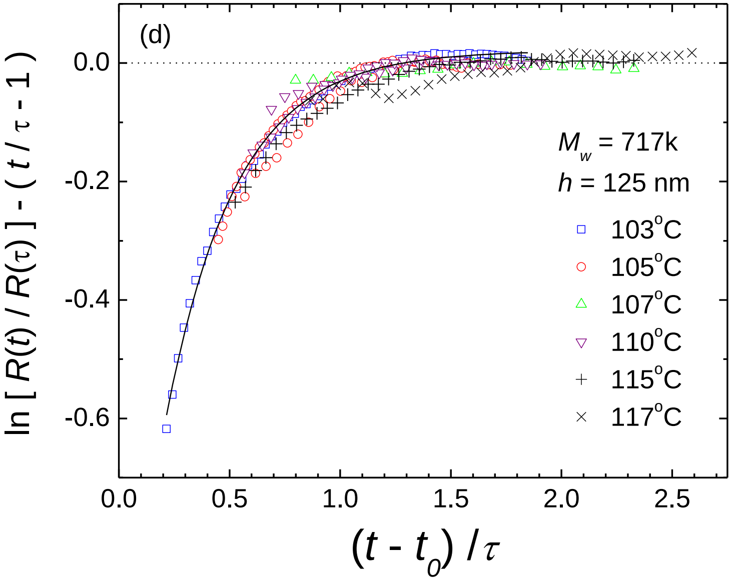


[Roth *et al*., PRE **72**, 021802 (2005)]

TRANSIENT BEHAVIOR







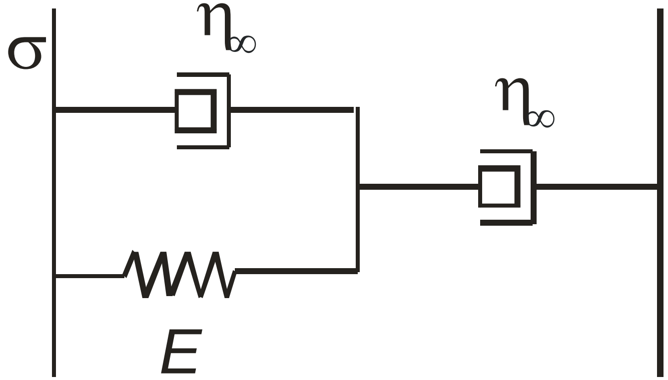
- scale axes: $\ln[R(t)/R(\tau)]$ vs t/τ
  - □ data sets coincide for $t > \tau$
- isolate transient
  - – single exponential decay time τ_1
- refer t to t_0 for which $R(t_0) = 0$
  - – overlap of data
  - – decay time τ_1 scales with τ

FITTING FUNCTION FOR *R*(*t*)

- empirically, *R*(*t*) data for all times well fit by
  - equivalent to time-dependent viscosity η(*t*)

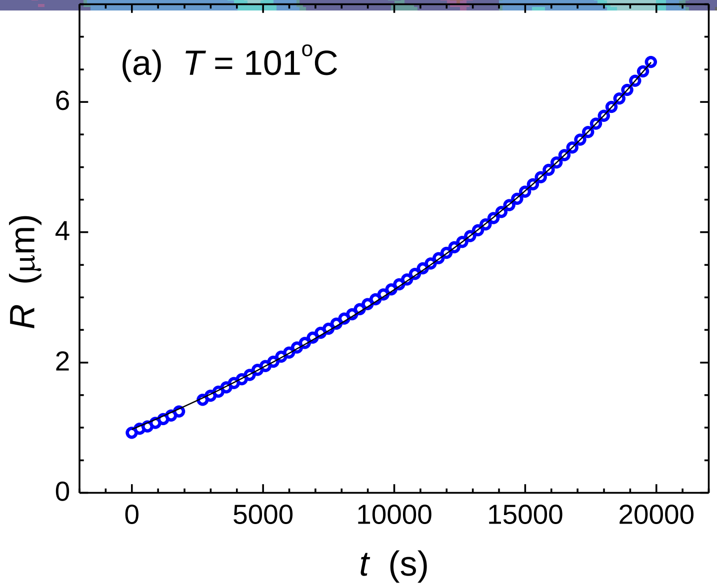
    where $\eta_\infty = \dfrac{\varepsilon\tau}{h}$ is viscosity for $t \gg \tau_1$

  - described by a three-component spring & dashpot model

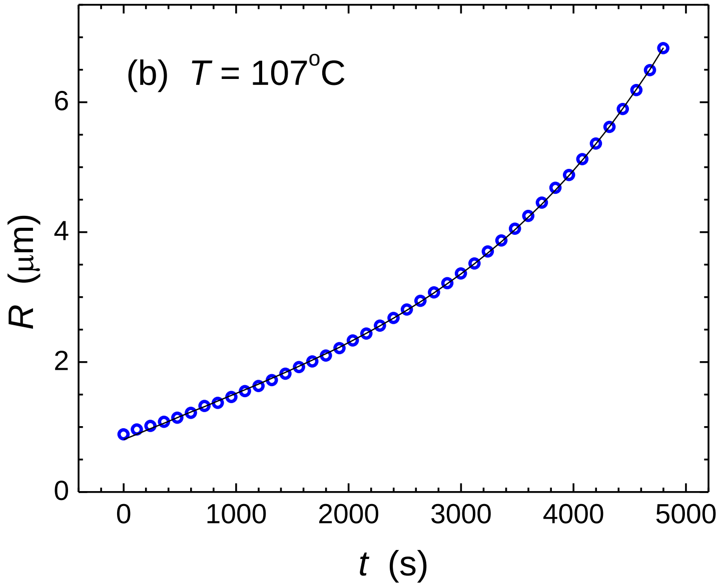


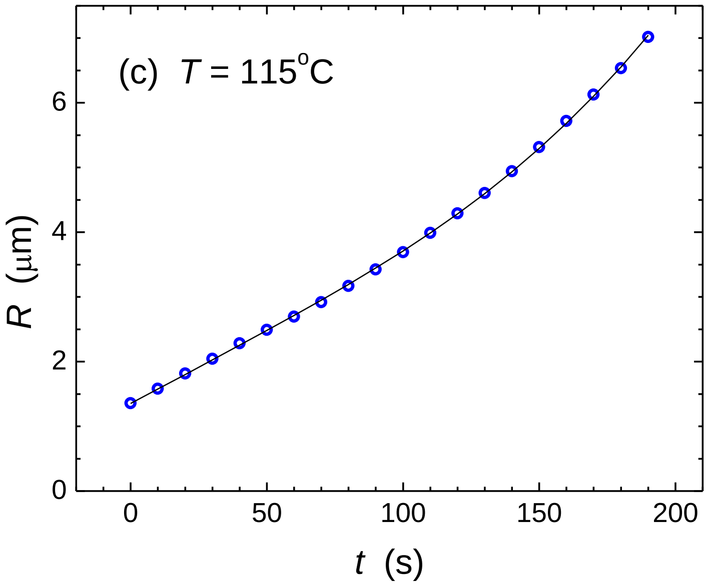
single relaxation time

FITS TO $R(t)$ DATA



- 3 fitting parameters:
  - R_0 value at start of measurements ($t = 0$)
  - τ exponential hole growth time
  - τ_1 longest relaxation time





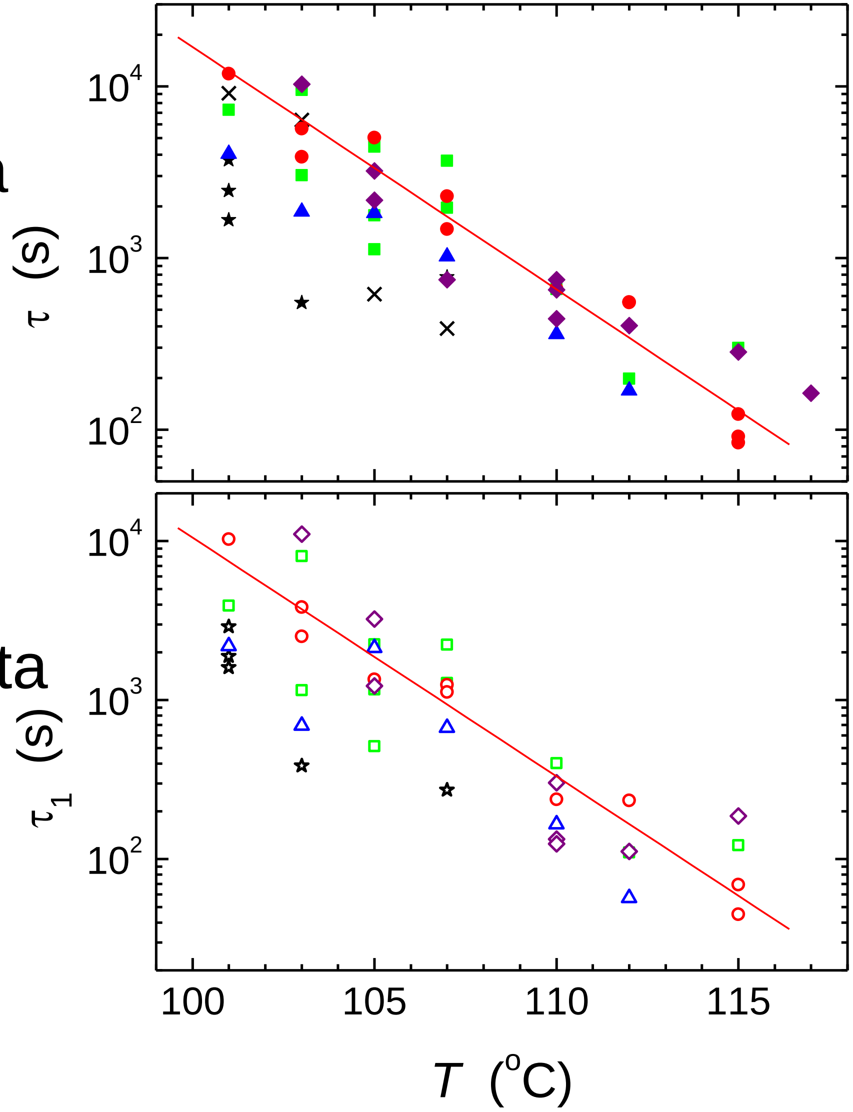
$M_w = 717 \times 10^3$

$h = 90$ nm

RELATIONSHIP BETWEEN τ AND τ_1

τ data

τ_1 data



- τ and τ_1 have similar temperature dependence with $\tau_1 \sim \tau/2$

  $[\tau/\tau_1 = 2.2 \pm 1.4]$

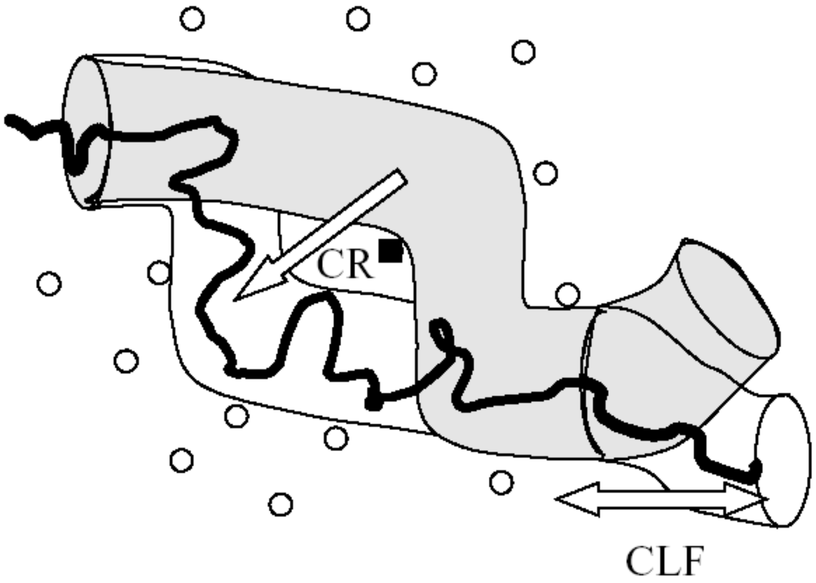
TUBE MODEL FOR POLYMER DYNAMICS

τ_d Reptation time
τ_R Rouse time

low shear rate	$\dot{\gamma} < \tau_d^{-1}$	reptation + contour length fluctuations (CLF)
intermediate shear rate	$\tau_d^{-1} < \dot{\gamma} < \tau_R^{-1}$	convective constraint release (CCR)
high shear rate	$\tau_R^{-1} < \dot{\gamma}$	chain stretch

Hole growth at $T = 101^{o}$C

$\tau_d^{-1} \sim 10^{-6} - 10^{-10}$ s^{-1}
$\tau_R^{-1} \sim 10^{-4} - 10^{-7}$ s^{-1}
$\dot{\gamma} \sim 10^{-4}$ s^{-1}



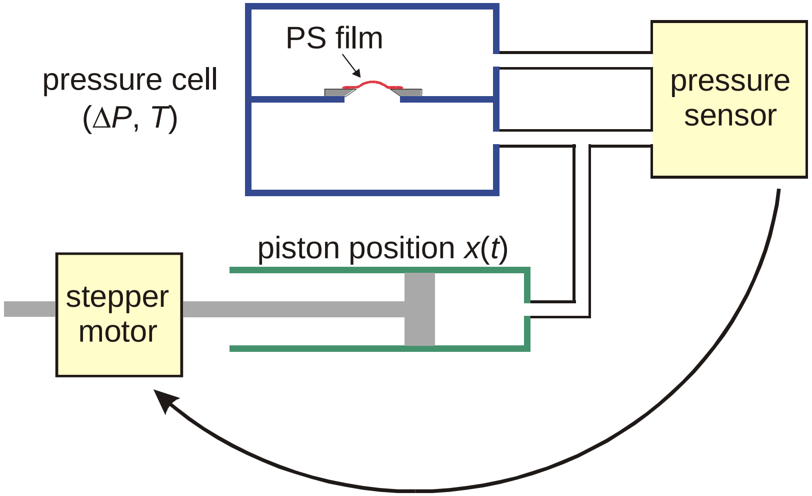
- hole growth at lowest temperatures occurs in the intermediate to high shear rate regimes
  - relaxation via CCR (no rotation in flow)
  - since $\dot{\gamma} = 2 / \tau$, expect $\tau_1 \sim \dot{\gamma}^{-1} \sim \tau / 2$
    → data consistent with CCR

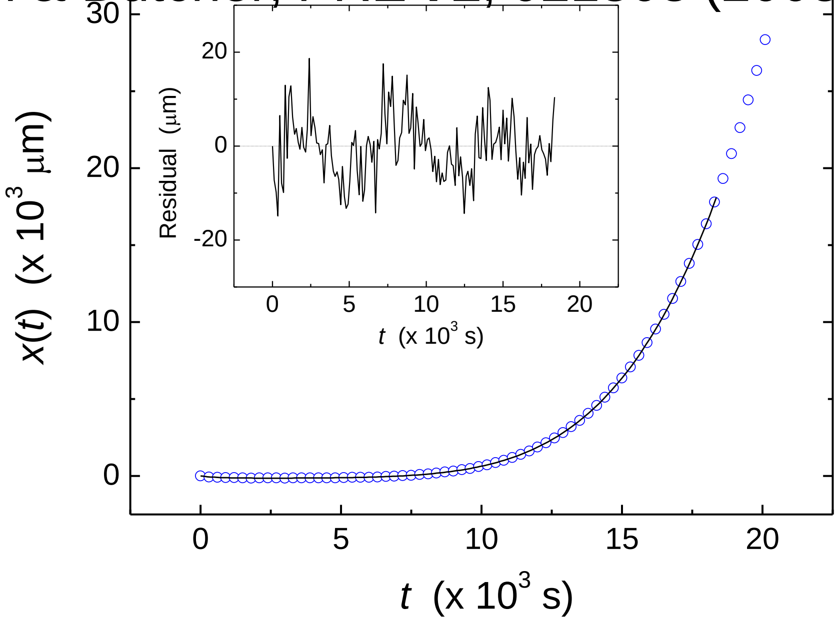
[Graham, Likhtman, McLeish, and Milner, J. Rheol (2003)]

DIFFERENTIAL PRESSURE EXPERIMENT

- differential pressure experiment

[Roth *et al.*, RSI **74**, 2796 (2003); Roth & Dutcher, PRE **72**, 021803 (2005)]





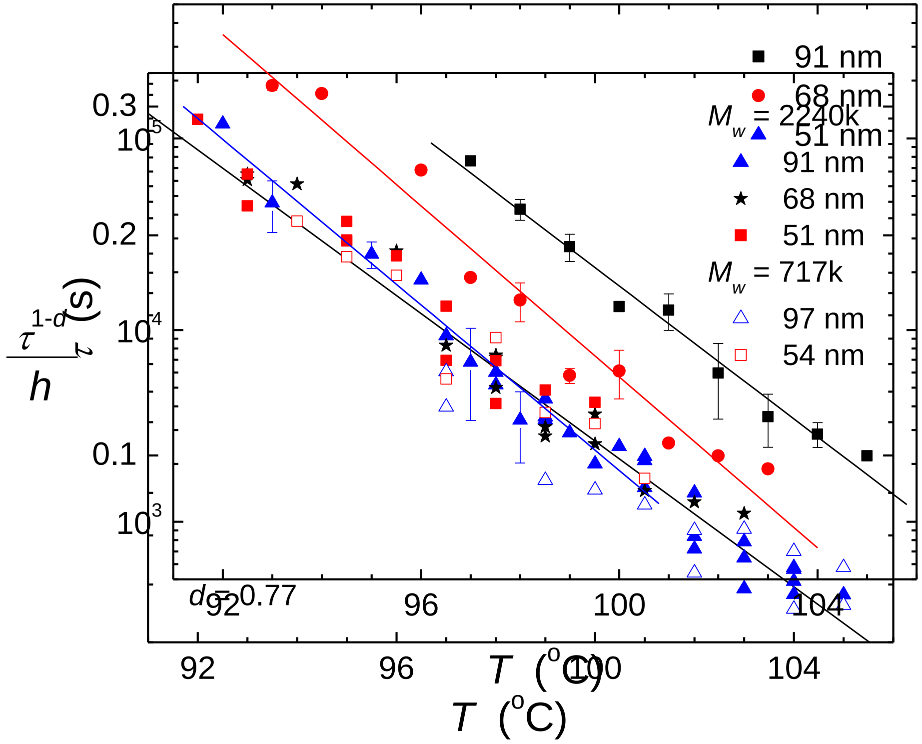
PS, M_w = 2240k, h = 69 nm, T = 98°C

– maintain pressure difference across PS film

– track piston position as a function of time

DPE RESULTS FOR FREELY-STANDING PS FILMS

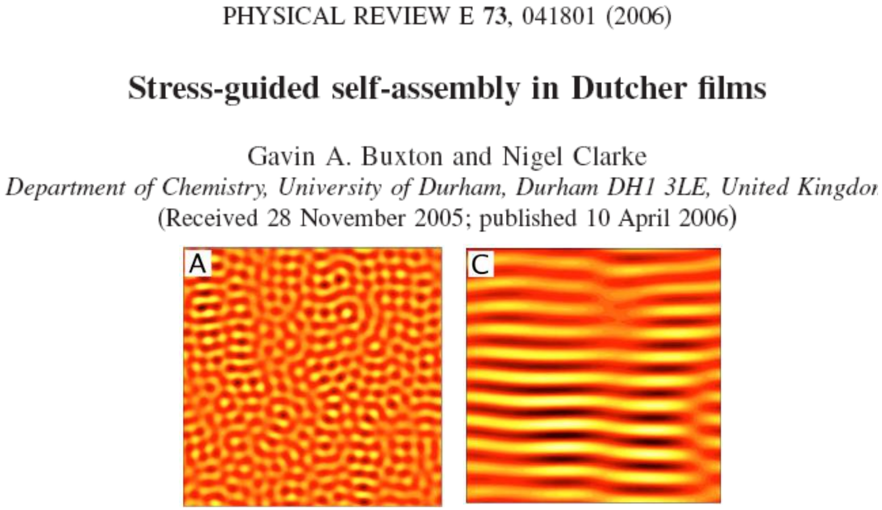
- temperature dependence of hole growth time τ
  - M_w = 717k, 2240k
  - 51 nm < h < 98 nm
  - 92°C < T < 105°C
  - consistent with shear thinning
  - despite large differences in T_g, onset temperature for hole formation is comparable to T_g^{bulk} for all films



[Roth *et al.*, RSI **74**, 2796 (2003); Roth & Dutcher, PRE **72**, 021803 (2005)]

FREELY-STANDING TRILAYER FILMS

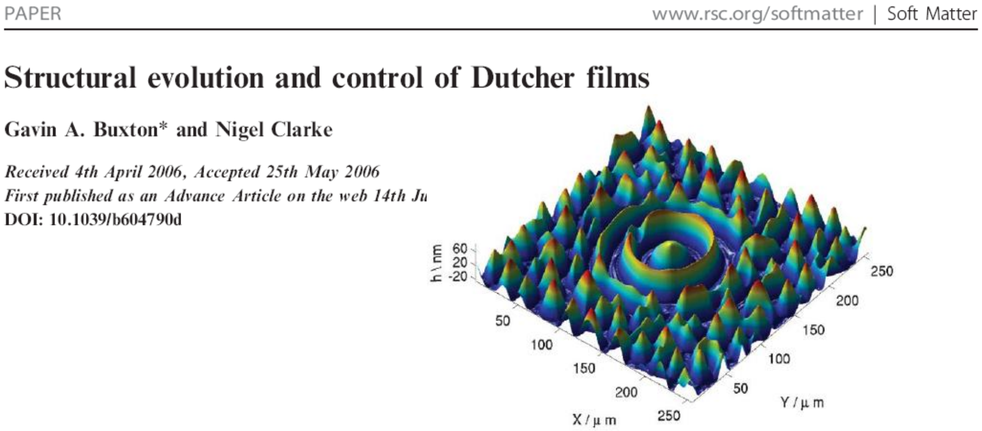
- trilayer films with central fluid layer and solid capping layers
  - – periodic lateral morphology forms upon heating due to amplification of thermal fluctuations



PHYSICAL REVIEW E **73**, 041801 (2006)

Stress-guided self-assembly in Dutcher films

Gavin A. Buxton and Nigel Clarke
Department of Chemistry, University of Durham, Durham DH1 3LE, United Kingdor
(Received 28 November 2005; published 10 April 2006)



PAPER www.rsc.org/softmatter | Soft Matter

Structural evolution and control of Dutcher films

Gavin A. Buxton* and Nigel Clarke

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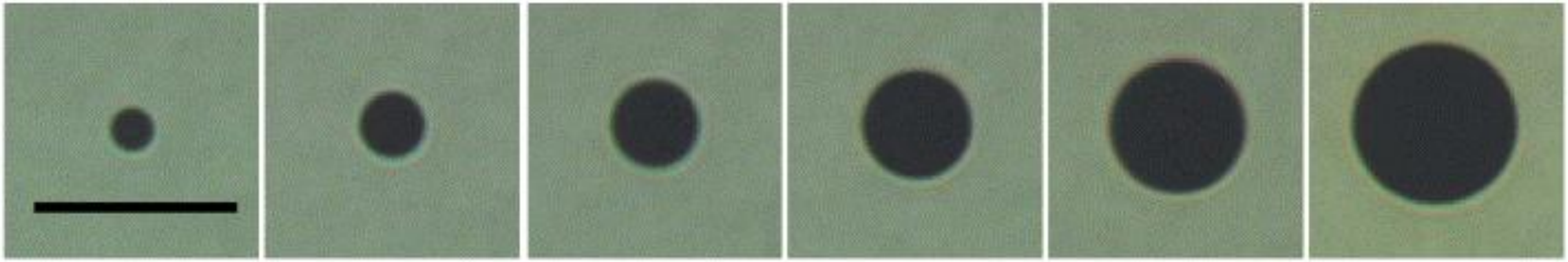
DOI: 10.1039/b604790d

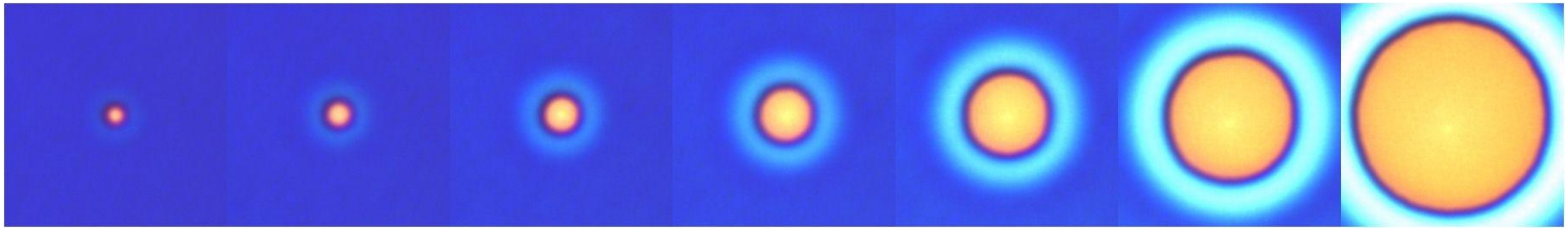
[C.A. Murray *et al*., PRE **69**, 061612 (2004)]

HOLE GROWTH IN PS/PI/PS TRILAYERS

- hole growth in PS freely-standing films
  - uniform thickening of films
  - absence of rim at edge of hole



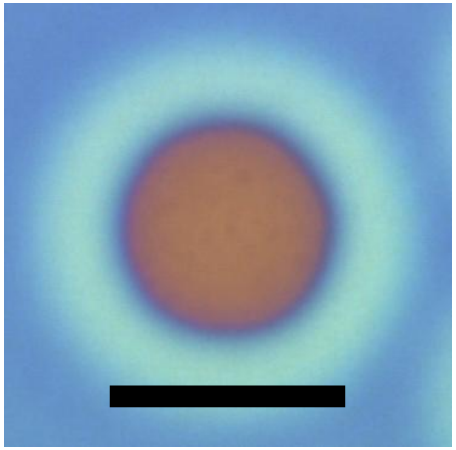
- hole growth in PS/PI/PS freely-standing films
  - holes form & grow in central PI layer
  - distinct rim at edge of hole



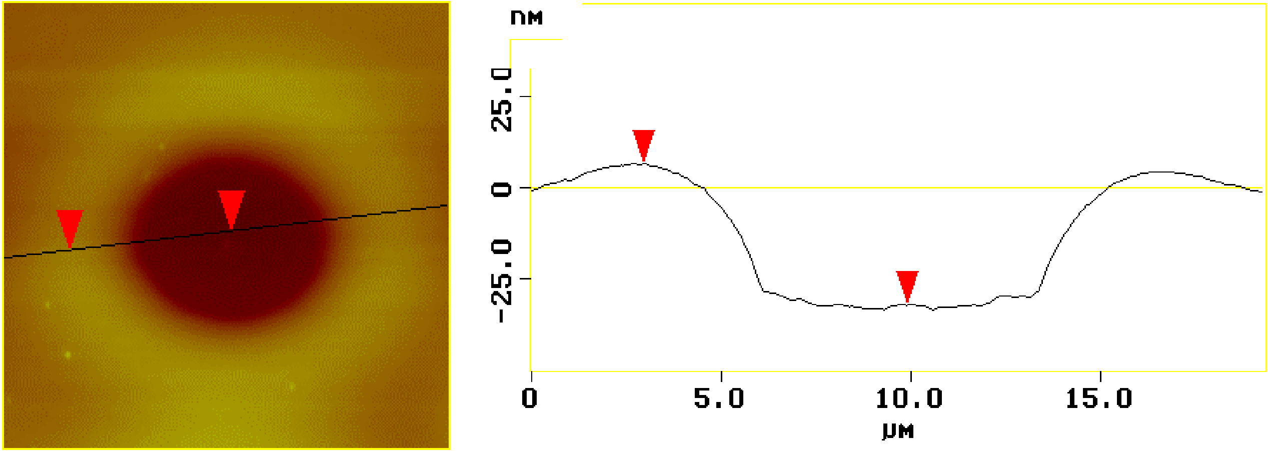
HOLE GROWTH IN PS/PI/PS TRILAYERS

- presence of rim verified using atomic force microscopy (AFM)

h = 50 nm, *L* = 75 nm



optical
microscopy



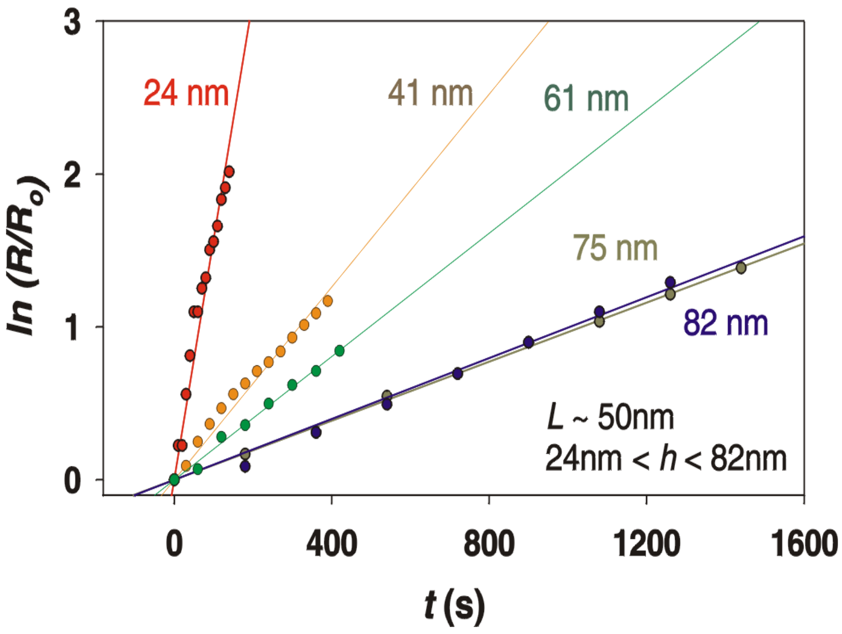
AFM

[C.A. Murray *et al*. (2006)]

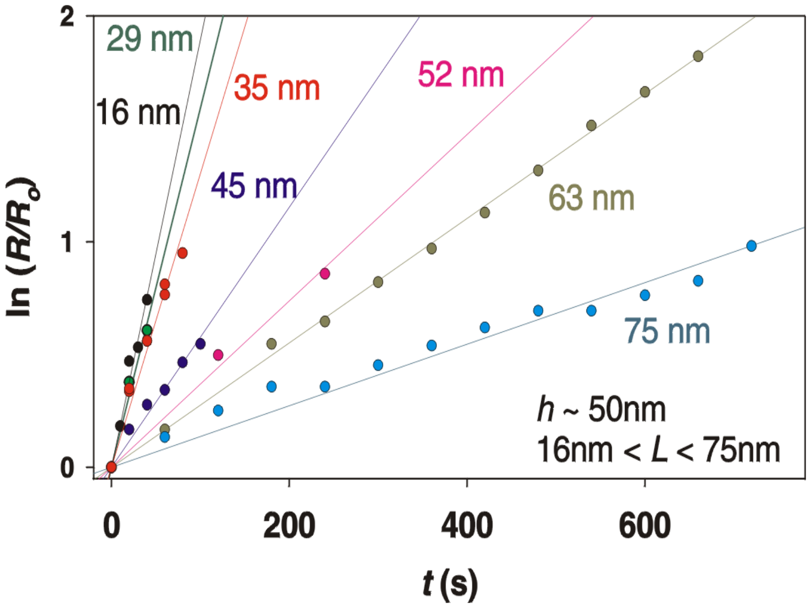
HOLE GROWTH IN PS/PI/PS TRILAYERS

- radius of hole in PI layer measured at fixed temperature

  T = 110ºC



fix PS thickness *L*
vary PI thickness *h*

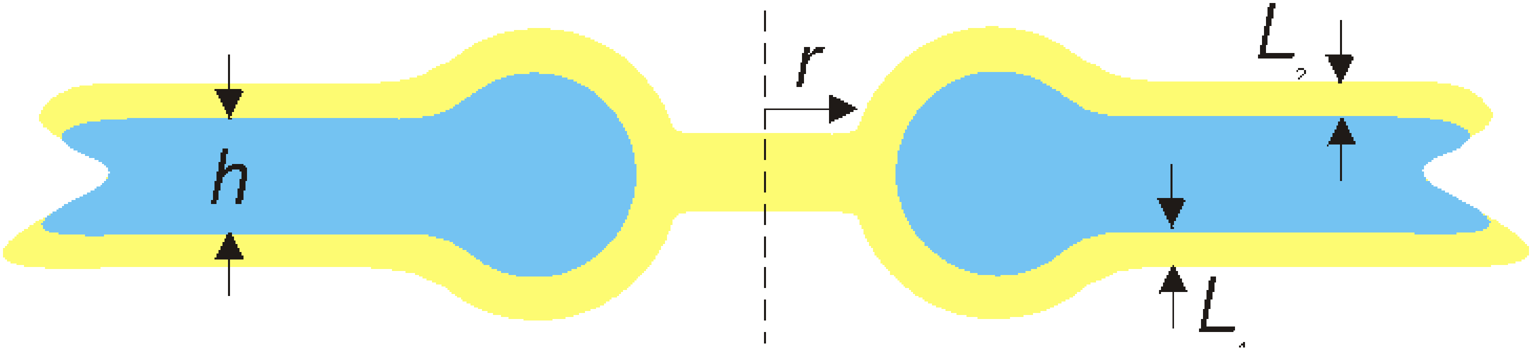


fix PI thickness *h*
vary PS thickness *L*

[C.A. Murray *et al*. (2006)]

HOLE GROWTH IN PS/PI/PS TRILAYERS

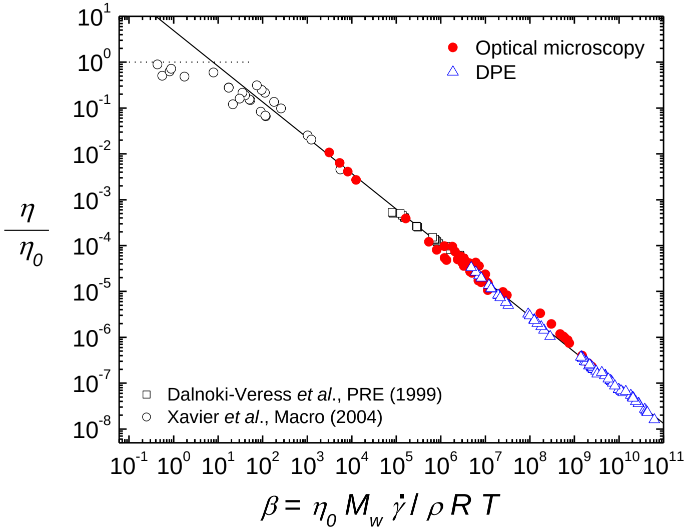
- relevant factors that determine hole growth in PI layer
  - surface & PS/PI interfacial energies
  - bending energy of PS layers
  - dispersion interaction between the PS/air interfaces



  - can understand slowing of hole growth with increase in *h* & *L*

SUMMARY

- hole growth in freely-standing PS films
  - two different experiments
    - shear thinning
    - convective constraint release
    - hole growth occurs at temperatures comparable to T_g^{bulk}
- hole growth in fs PS/PI/PS films
  - qualitatively different hole growth
    - hole growth in PI determined by PS



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