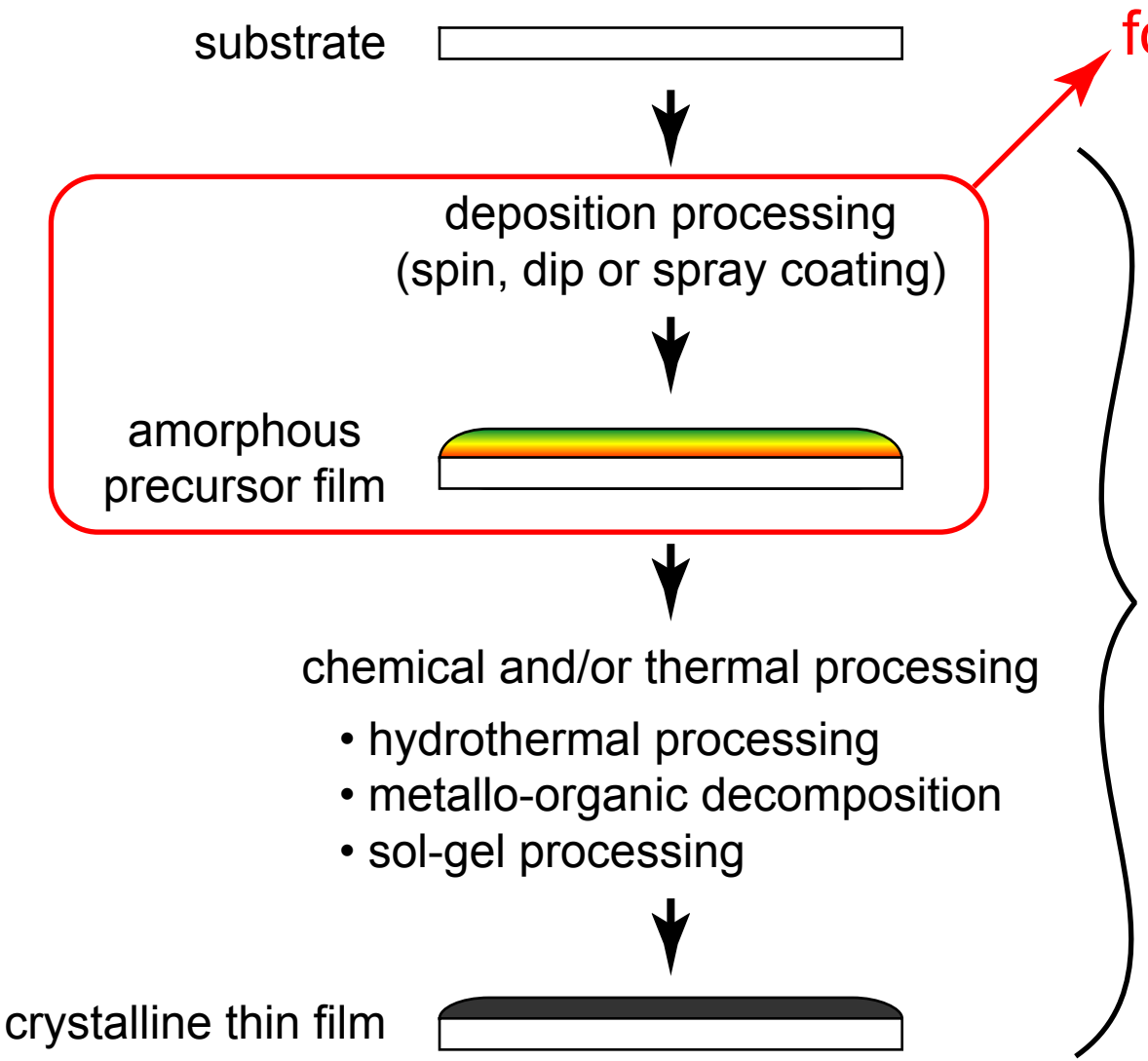
Precursor Routes to Ceramic Thin Films



Film cracking is observed above a critical film thickness (h_c).

h_c = 0.5 - 1.0 μm (typically)

The Critical Thickness and Fracture Toughness of Thin Metal-Organic Precursor Films

- optical interference technique for measuring h_c
- processing effects on h_c
- relating h_c to film fracture toughness

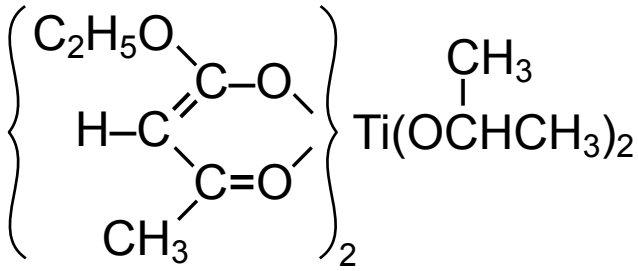
Adapted from:

R.K. Roeder and E.B. Slamovich, "Measuring the critical thickness of thin metal-organic precursor films," *J. Mater. Res.*, **14** [6] 2364-2368 (1999).

R.K. Roeder and E.B. Slamovich, "Assessment of the Critical Thickness and Fracture Toughness of Thin Metal-Organic Precursor Films," *Ceram. Trans.*, **83**, 375-382 (1998).

Precursor and Precursor Solutions

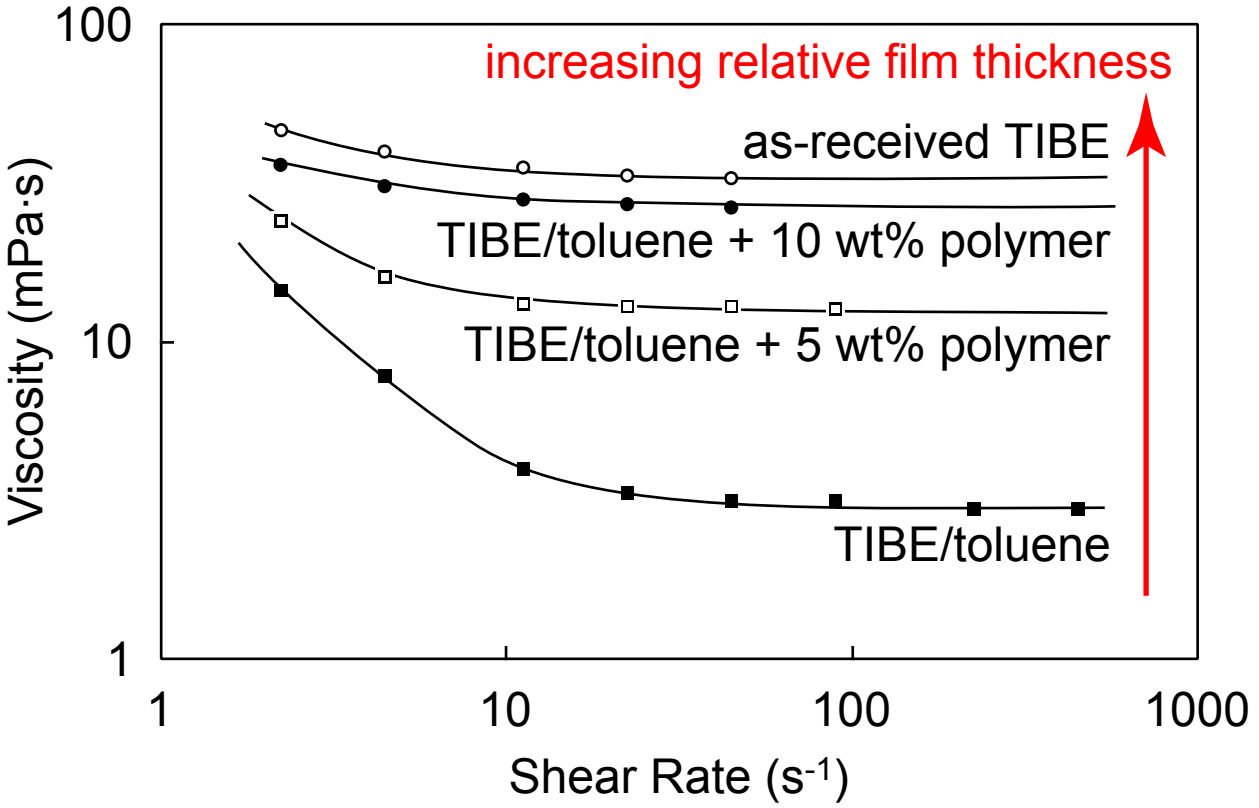
TIBE

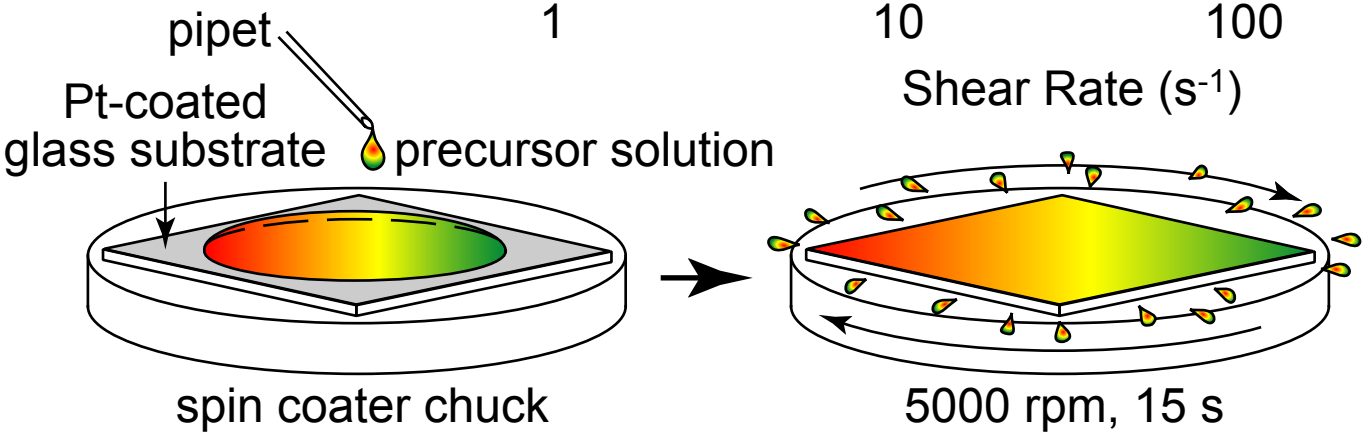


Precursor	Solvent	Polymer
TIBE	none	none
TIBE	50 vol% toluene	none
TIBE	50 vol% toluene	5 wt%*
TIBE	50 vol% toluene	10 wt%*

* Kraton D1102C, stryrene-butadiene-styrene block co-polymer, added in wt% relative to the precursor.

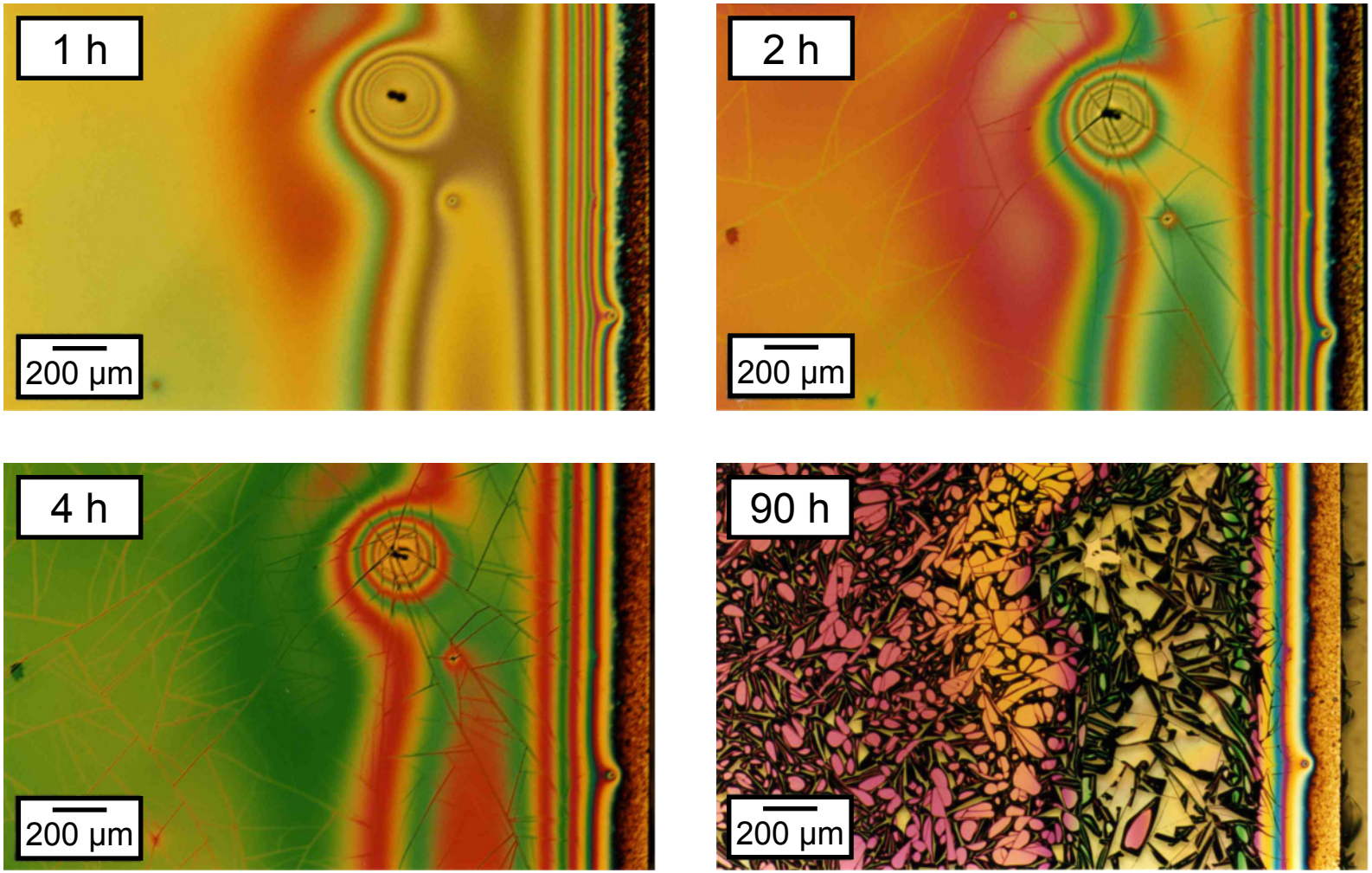
Spin Coating





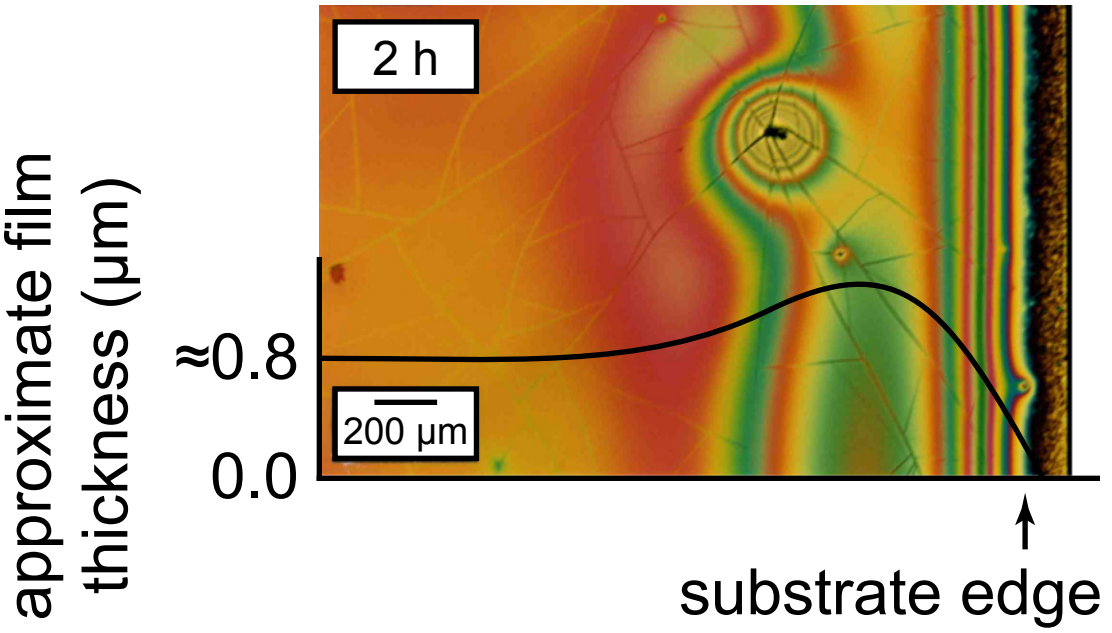
Crack Initiation and Growth

TIBE - 50 vol% toluene - no polymer



Film Thickness Profile After Spin Coating

TIBE - 50 vol% toluene - no polymer



Crack Initiation and Growth

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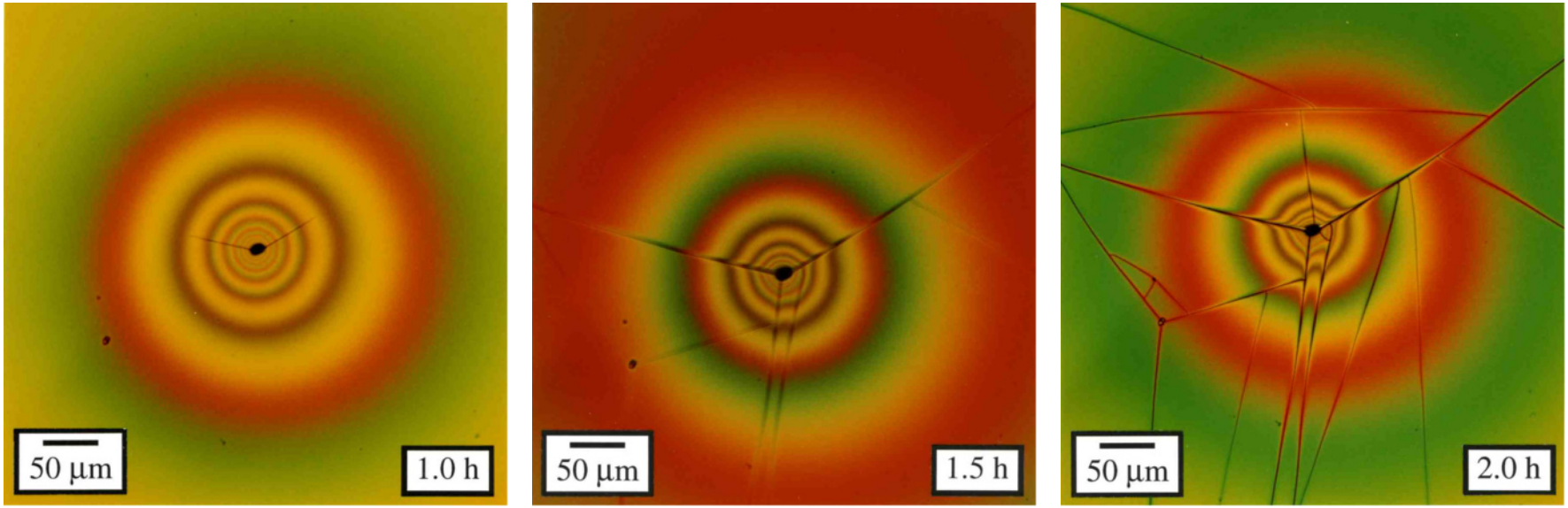
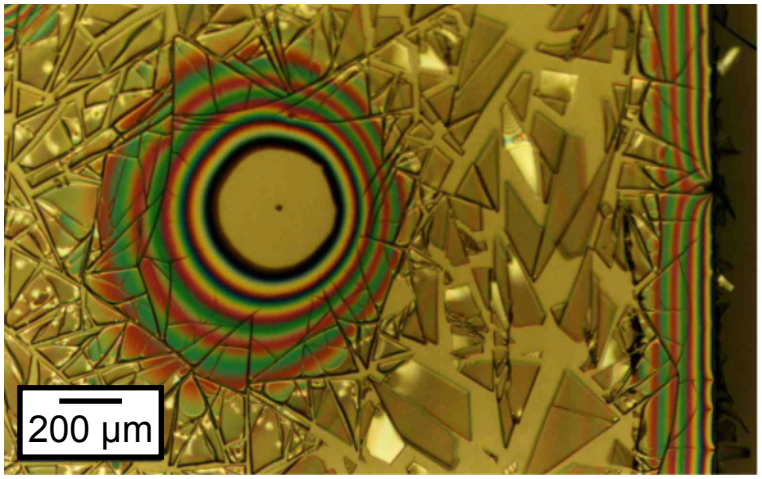
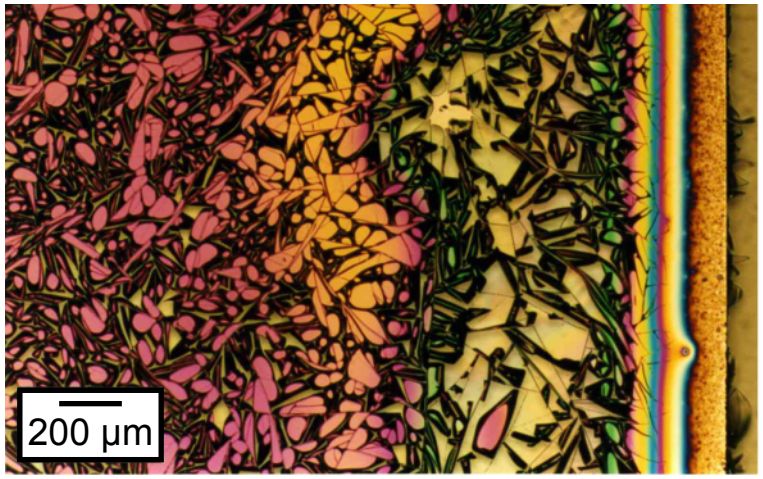


Film Cracking After 90 h Drying

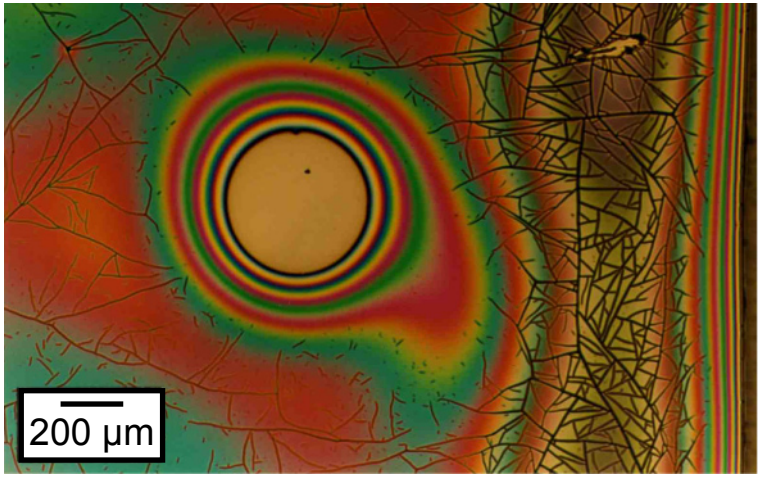
TIBE



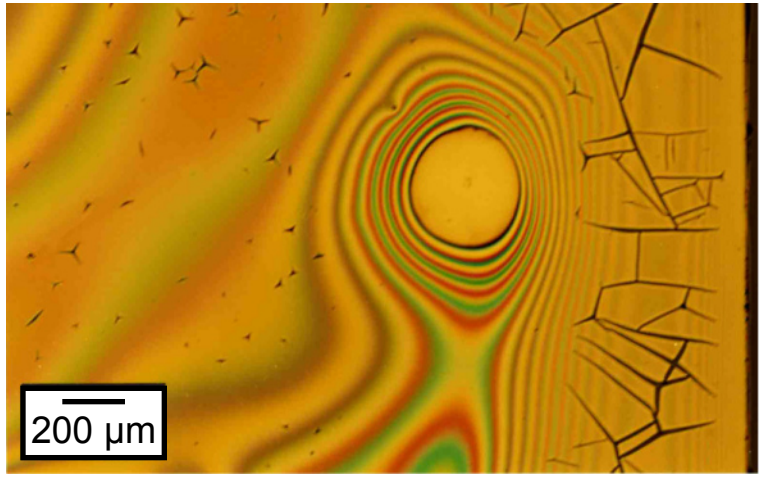
TIBE + 50 vol% toluene



+ 5 wt% polymer

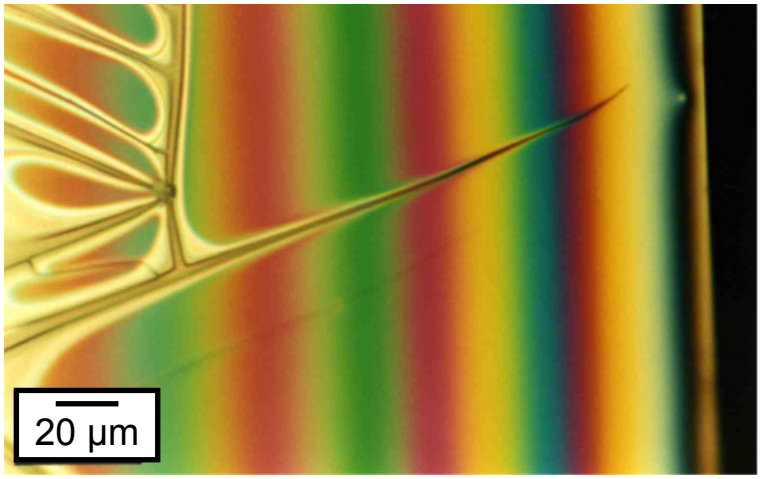


+ 10 wt% polymer

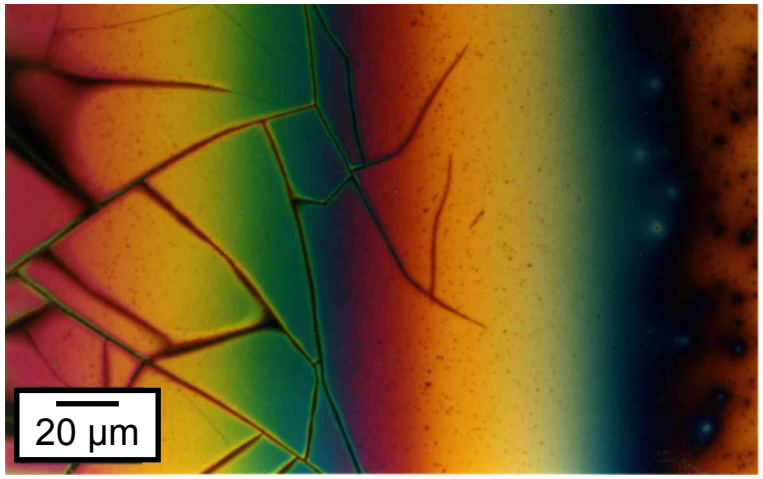


Film Cracking After 90 h Drying

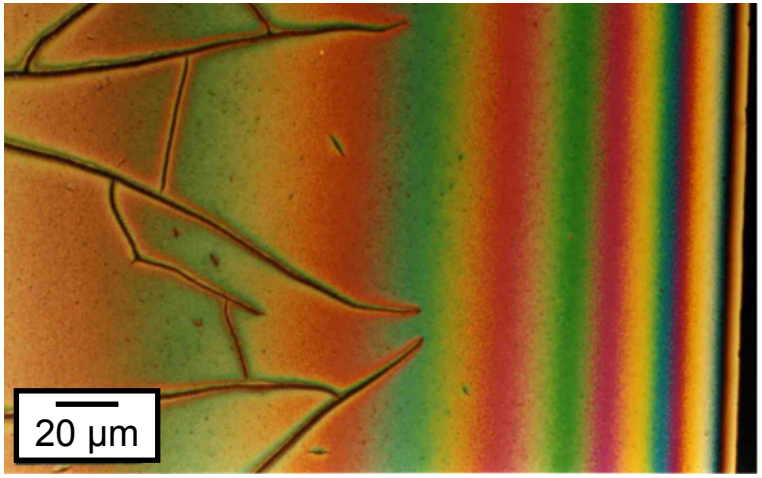
TIBE



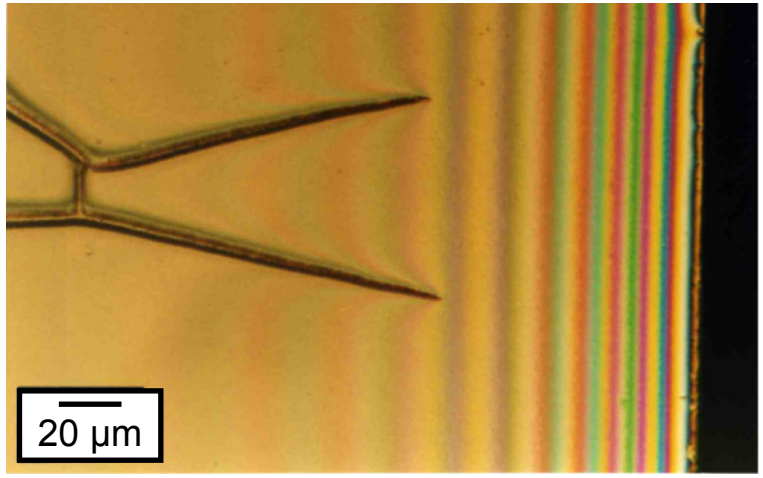
TIBE + 50 vol% toluene



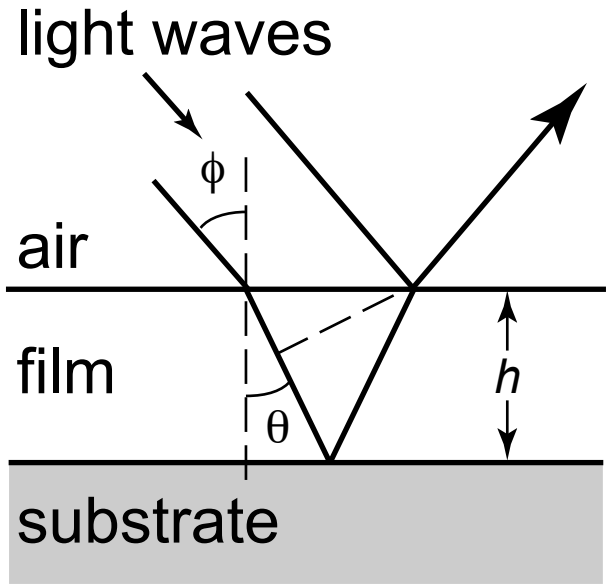
+ 5 wt% polymer



+ 10 wt% polymer



Optical Interference



h = film thickness
$\boldsymbol{n}$ = film refractive index
λ = wavelength of light
ϕ = angle of incidence
θ = angle of refraction
m = wave order

- if refractive index of substrate > film > air:
  path difference = $2h(\boldsymbol{n}^2 - \sin^2\phi)^{1/2}$
- for light normal to film ($\phi = 0°$):
  constructive interference, $m\cdot\lambda = 2\boldsymbol{n}\cdot h$
  retardation, $\delta = 2\boldsymbol{n}\cdot h$
  film thickness, $h = m\cdot\lambda/2\boldsymbol{n} = \delta/2\boldsymbol{n}$

Isochromatic Color Fringe Chart

Calculated using $\boldsymbol{n}$ = 1.522 for TIBE.

m	color fringe	δ (nm)	h (μm)
1	black	0	0.000
	iron gray	50	0.016
	gray	100	0.033
	gray blue	160	0.053
	white	260	0.085
	yellow	330	0.108
	yellow brown	440	0.145
	orange red	500	0.164
	red	540	0.177
2	violet	580	0.191
	blue	680	0.223
	blue green	720	0.237
	green	750	0.246
	yellow green	840	0.276
	yellow	920	0.302
	orange red	1000	0.329
	violet red	1050	0.345
	violet	1100	0.361
3	blue	1150	0.378
	blue green	1250	0.411
	green	1350	0.443
	yellow green	1400	0.460
	yellow	1450	0.476
	rose red	1500	0.493
	carmine	1550	0.509
	violet gray	1650	0.542
4	blue gray	1700	0.558
	blue green	1750	0.575
	green brown	1800	0.591
	pale green	1900	0.624
	pale gray	2000	0.657
	pale red violet	2200	0.723
5	pale green	2500	0.821
	pink	2700	0.887
	and so on...		

Critical Thickness of Precursor Films

- Define h_c as the film thickness where cracks neither initiate nor propagate.
- Utilize film thickness variations.
- Measure h_c from the color fringe where propagating cracks arrest.

solvent	polymer (wt%)	nearest observed fringe color	m	h_c (μm)
none	0	yellow	1	0.10 ± 0.01
toluene	0	yellow	1	0.11 ± 0.01
toluene	5	red	3	0.51 ± 0.05
toluene	10	pink/pale green	5/6	0.92 ± 0.09

Film Thickness Measurement Using Isochromatic Color Fringes from Reflected Light

advantages:

- simple, requires conventional optical microscope
- “contour map” of film thickness
- simultaneous observation of cracking and film thickness

disadvantages:

- must know refractive index of film
- up to 10% error

Sources of Error in h_c Measurement

assumptions:

- no light absorption by film or substrate (phase shift on reflection of exactly 0 or $\lambda/2$)
- constant ***n*** with time, λ and polymer addition
- light incident normal to film surface

Error increases with increasing objective lens numerical aperture (higher magnification).

NA = 0.4 - 0.8	several % error in *h*
NA ≥ 0.9	up to 10% error in *h*

Relating h_c to Fracture Toughness

$$h_c = \left(\frac{K_c}{\sigma \cdot \Omega} \right)^2$$

h_c = critical film thickness

K_c = critical stress intensity factor

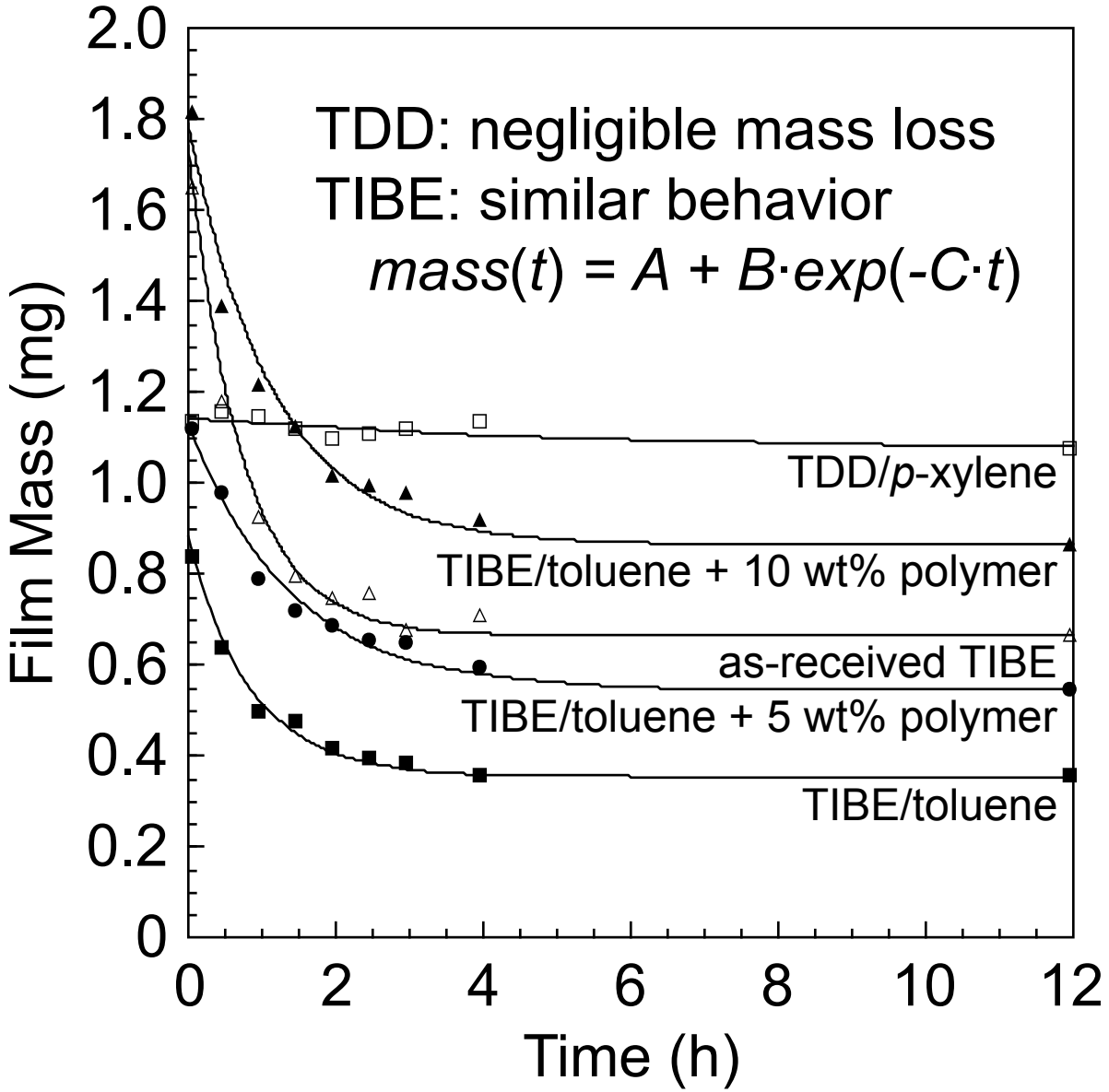
where $\Omega \propto \sqrt{\pi \cdot (E_f / E_s)}$

A.G. Evans, *et al.*, *J. Mater. Res.*, **3** [5] 1043-1049 (1988).
M.S. Hu and A.G. Evans, *Acta Metall.*, **37** [3] 917-925 (1989).

Therefore, a measure of the film stress is needed:

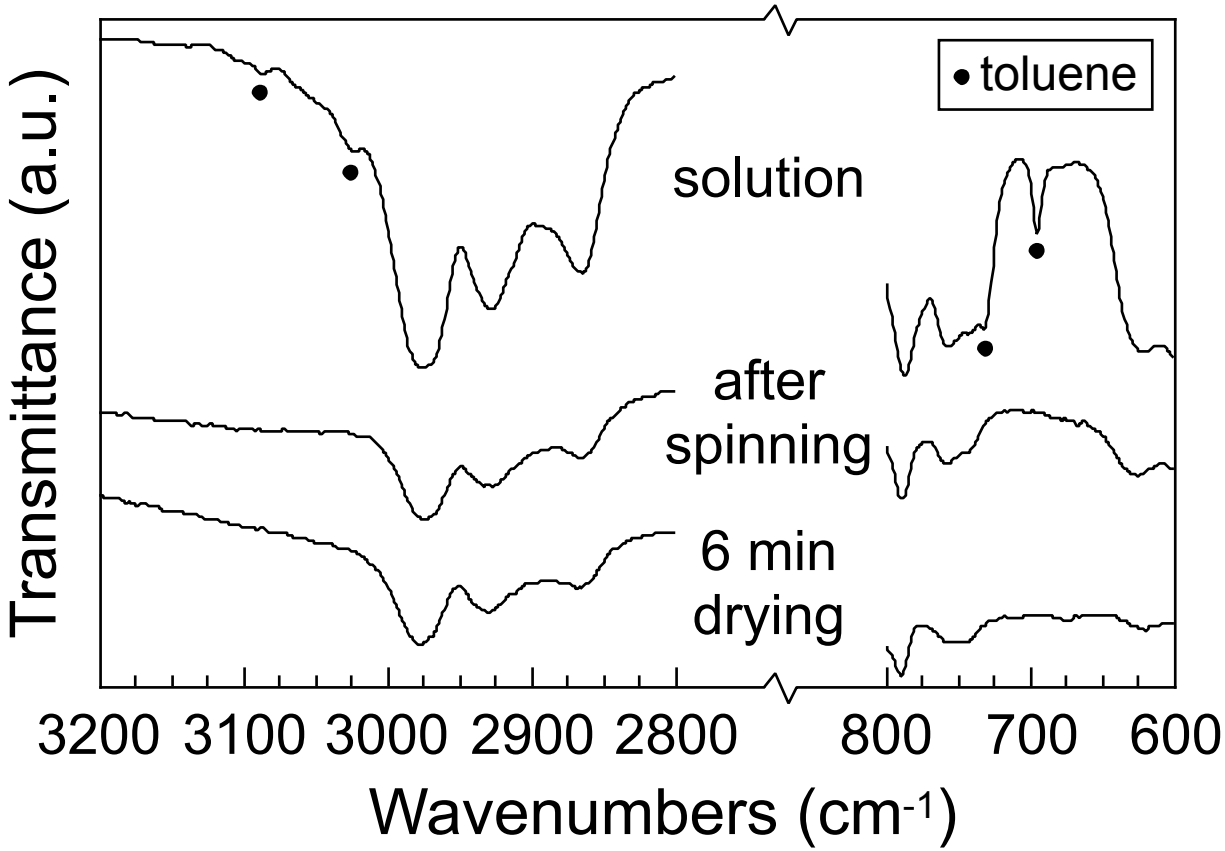
- Measure substrate curvature using ellipsometry or laser techniques.
- Measure mass loss during drying.
  $\Rightarrow$ Calculate volume shrinkage.
  $\Rightarrow$ Calculate linear strain.
  $\Rightarrow$ Calculate film stress assuming linear elasticity.

Film Mass Loss



Origin of Mass Loss: FT-IR

e.g., TIBE - 50 vol% toluene - no polymer

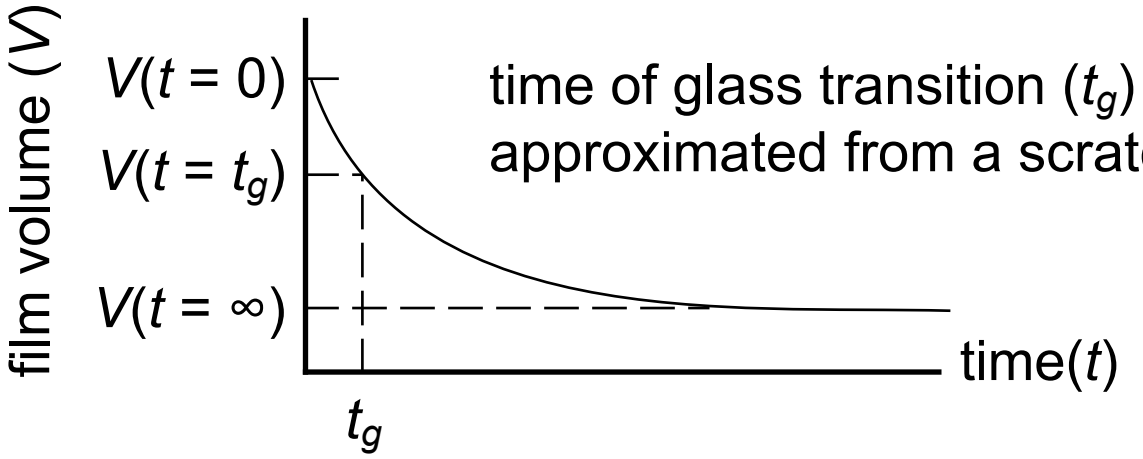


Origin of Mass Loss: Relative Volatility

	molecule	boiling point (°C)
	toluene	111
	p-xylene	138
TIBE	ethyl acetoacetone	181
TIBE	titanium isopropoxide	232
TDD	neodecanoic acid	250-257
TDD	titanium methoxide	>300

Estimation of Film Stress From Mass Loss

$\Rightarrow$ Convert measured film *mass*(t) to film *volume*(t).



$$\Rightarrow \varepsilon = \frac{\Delta L}{L} = \left(1 + \frac{\Delta V}{V}\right)^{1/3} - 1 \longrightarrow \varepsilon(t_g) = \left(1 + \frac{V(t_g) - V_\infty}{V(t_g)}\right)^{1/3} - 1$$

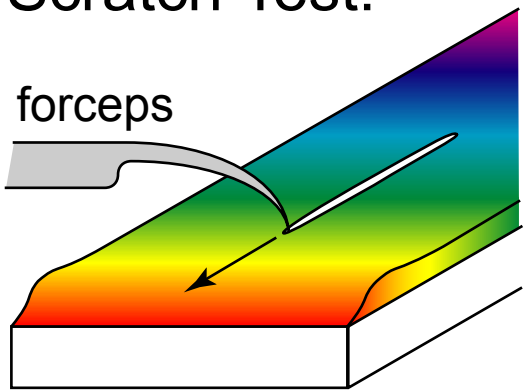
$$\Rightarrow \frac{\sigma(t_g)}{E} = \frac{\varepsilon(t_g)}{1 - \nu}$$

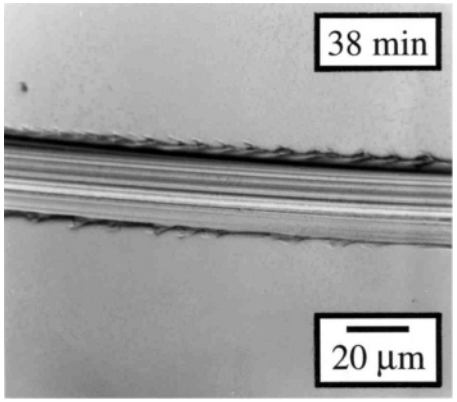
$$\Rightarrow \frac{K_{Ic}}{E}(t_g) = \Omega \cdot \frac{\varepsilon(t_g)}{1 - \nu} \cdot h_c^{1/2}$$ relative fracture toughness, $K' = \dfrac{\frac{K_{Ic}}{E}(t_g)}{\frac{K_{Ic}}{E}(t_g)_{\text{TIBE}}}$

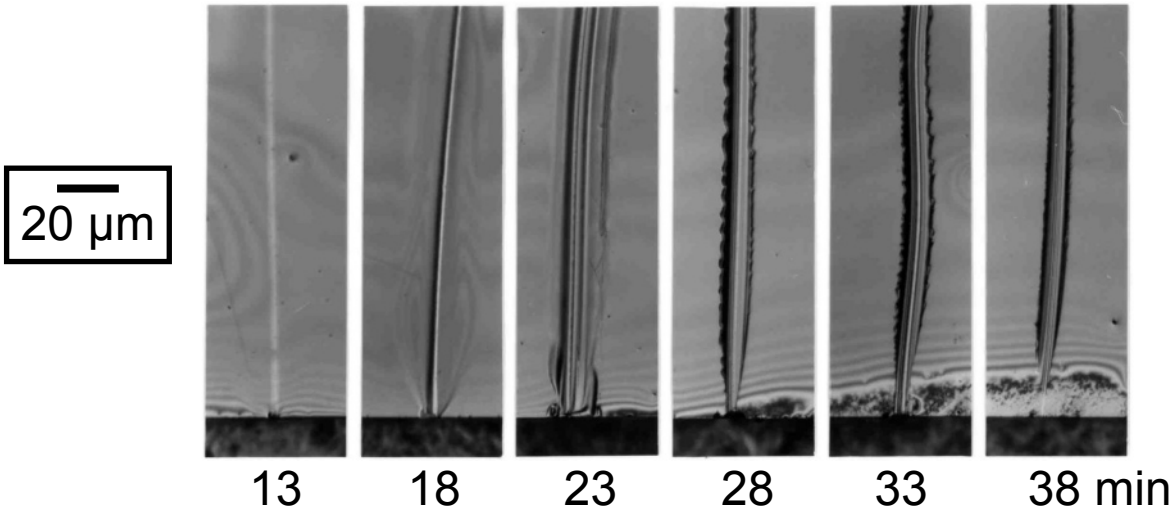
Precursor Film Glass Transition

TIBE - 50 vol% toluene - no polymer

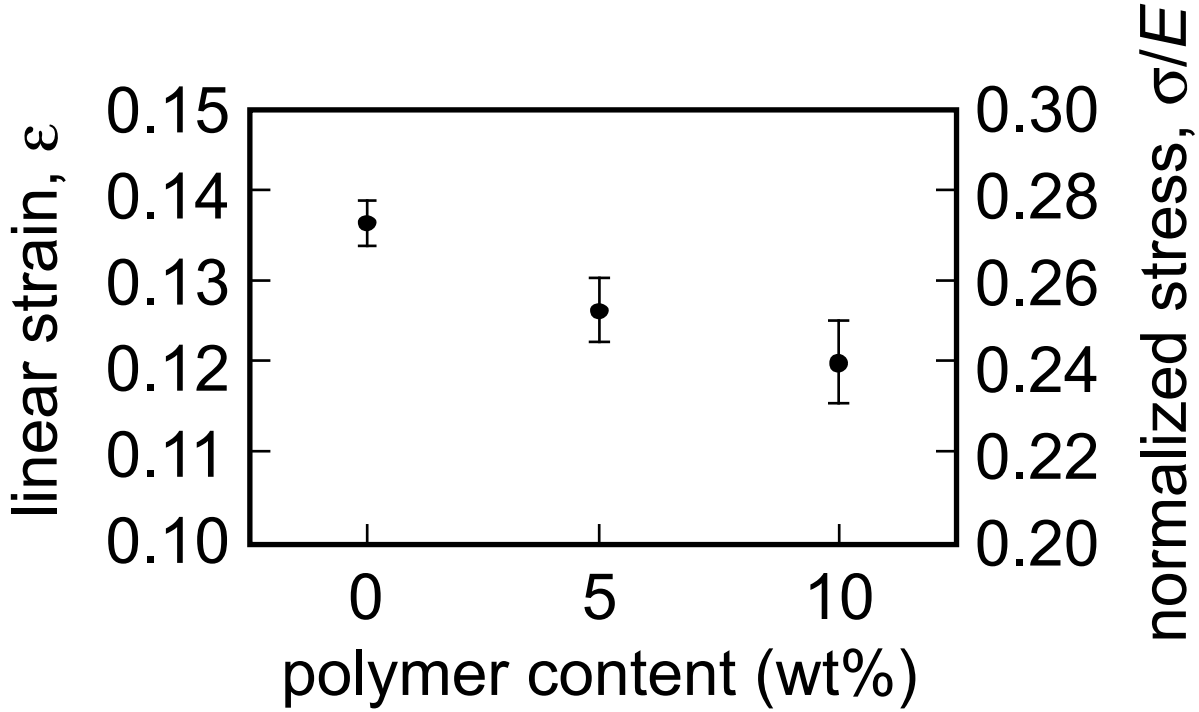
Scratch Test:



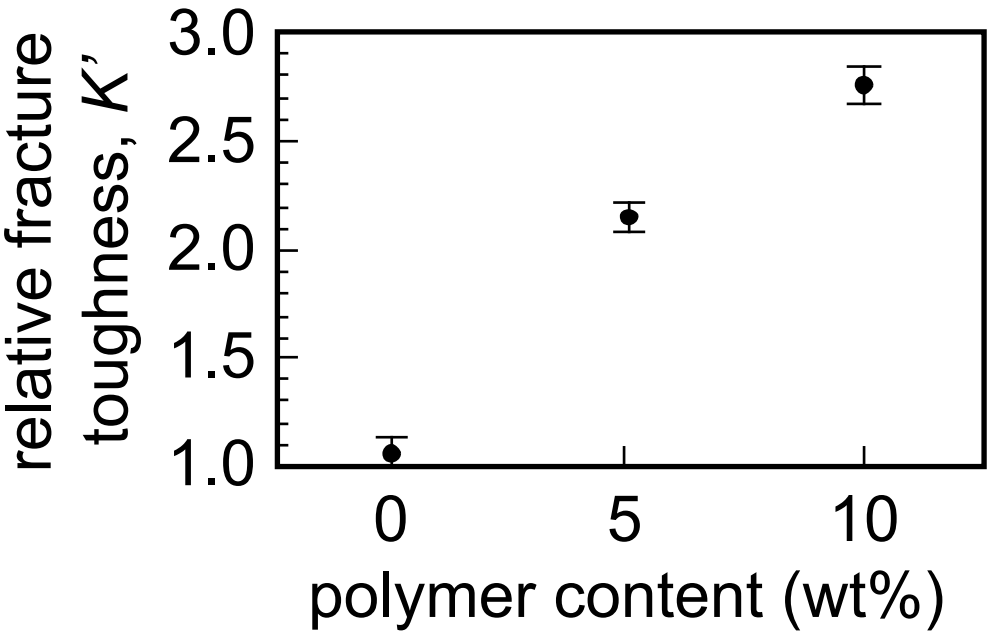




Relative Film Stress



Relative Film Fracture Toughness



Summary

- The cracking and thickness of thin metal-organic precursor films were simultaneously observed during drying using a conventional optical microscope.
- Film thickness was monitored using isochromatic color fringes produced by interference of reflected white light.
- The critical film thickness was determined by the color fringe corresponding to the location where cracks arrested.
- The addition of small amounts of an elastomeric polymer to precursor solutions increased the critical film thickness by toughening films.
- Combining the critical thickness measurement technique with stress measurements could allow precise measurement of thin film fracture toughness.

Fracture of Materials Can be Artistic!