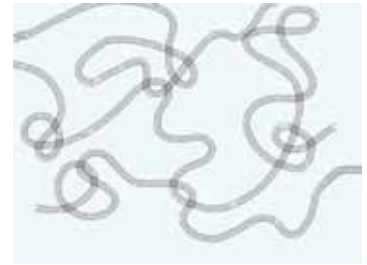# Mesoscopic physical behavior of macromolecules in ultrathin films

由奈米薄膜的不穩態研究長鏈高分子
在奈米尺度的物理性質

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高分子之介觀與奈米性質

- 高分子薄膜,在現代人的生活以及人類高科技的發展,佔據著關鍵的地位.隨著科技能力的進步與實際應用的需求,薄膜的厚度已進入奈米尺度的範圍 (1nm < 厚度< 100nm).

- 高分子是小分子以類似頭接尾的方式,共價鍵結而成.分子量可以高達數百萬以上,分子的長度可至200 microns以上.在自然放鬆的情況下,高分子呈蓬鬆的毛線球狀 (random walk),其半徑(R_g)約可達30 nm. (30 chains sharing the same volume)

- 在奈米薄膜中,當薄膜厚度接近或小於分子團的直徑時,分子鏈的組態 (conformation)將與既知之情況大大不同.

- 分子鏈的組態,影響到長分子鏈之堆積,分子鏈之間的交纏,分子鏈的運動,以及發光高分子受外在光照射或電場激發下能量的傳遞.

- 高分子在介觀以及奈米尺度之物理行為與分子堆積的方式,仍有許多不清楚的地方,如玻璃轉換現象(glass transition),高分子發光及能量轉移機制,高分子在玻璃態的運動,高分子在界面的結構與運動方式,高分子組態與堆積,高分子交纏網路的結構,高分子與界面的摩擦,等等,都是目前高分子科學家未解,但極感興趣的問題.

高分子奈米薄膜

- 組態之不同,不單只是分子幾何堆積方式的變化,更牽涉奈米薄膜之成膜過程.
    - Spin coating: 最常用的主流方法
    - Dip coating (not going to work for c*以製備高分子薄膜)
    - 電漿聚合高分子薄膜(crosslinked system), 熱蒸鍍高分子薄膜

- 稀薄高分子溶液在旋塗過程中,懸浮高分子團受離心力之張扯,在形變與回復之中,鋪為液體薄膜,進而隨溶劑的快速揮發,固化為玻璃態的薄膜.

- 根據計算,在仍有15%的溶劑濃度時,液體薄膜已進入玻璃態,此時之後,高分子團在此溶液中的鬆弛,溶劑揮發速度的快慢以及在奈米尺度的均勻度-是否會受分子交纏密度的影響,以及最後薄膜內分子局部交纏是否會受到溶劑揮發均勻性不一的影響,都將強烈影響高分子在奈米薄膜之分子組態.

1. S. Herminghaus, K. Jacobs, K. Mecke, J. Bischof, A. Fery, M. Ibn-Elhaj, S. Schlagowski, *Science* (1998).
2. R. Seemann, S. Herminghaus, K. Jacobs, *Phys. Rev. Lett.* (2001).
3. G. Reiter, P.G. de Gennes, *Euro. Phys. J. E* (2001); F. Saulnier, E. Raphael, P.-G. de Gennes, *Phys. Rev. Lett.* (2002).
4. J. C. Daniel, R. Audebert, "*Soft Matter Physics*", M. Daoud and C.E. Williams (Eds.), Ch. 3 (1995).

分子作用力

- 若拘束於奈米薄膜內,凝凍於玻璃態的高分子之分子組態偏離平衡態,則當溫度上升時,分子團會反彈. 此分子反彈力(molecular recoiling force),和高分子的組態有關. 任何有關分子反彈力和分子組態的直接資訊,對於我們了解高分子鏈在奈米尺度的機械行為,如黏彈性運動,以及分子交纏的性質,會帶來直接的重要突破.
  - 分子反彈力造成高分子薄膜的不穩定.
  - 非常少的研究涉及此高分子的反彈力.

- 除了分子反彈力之外,奈米薄膜的表面張力(capillary force), $\gamma\tau$,約為其重力,$\rho g\tau$,的一萬倍. 此表面張力,主要的來源為長距離凡德瓦爾力, $\sim A/\tau^2$,以及酸鹼力, 構成另一個作用於奈米薄膜內高分子團的外力,也強烈地影響分子組態以及高分子奈米薄膜的性質[1-4]. (*A*: Hamaker constant; τ: film thickness)

Approaches

- 高分子薄膜除潤研究: 分子力的量測

- 分子鏈奈米光學性質
- 高分子鏈-奈米碳管在奈米複材之交互作用-奈米增韌機制
- 奈米薄膜機械性質與分子鏈擴散行為
- 奈米奈米薄膜與界面摩擦

Outline

◆ **Part 1:** Molecular Recoiling Force

◆ **Part 2:** Total molecular forces operative in thin films

◆ **Part 3:** Excess free energy of ultrathin films

◆ **Part 4:** Enhancement of luminescence of dewet conjugated polymer films

◆ **Part 5:** Mechanical coupling between polymer thin film and substrate: the 2nd-stage dewetting

高分子薄膜除潤 - 簡介

- 高分子薄膜目前已廣泛應用在許多範疇，包括塗層、介電 層、潤滑、半導體元件、發光元件、生物感測元件等，故其在固體基材上的穩定性就扮演相當重要的角色。

- 一般而言，當高分子薄膜厚度低於100nm，並於玻璃轉換溫度之上熱處理時，即產生破裂，原本平整的薄膜會分裂成液滴狀(droplets)的圖樣，這就是所謂的dewetting(除潤現象)。

The liquid film on high-energy surface.
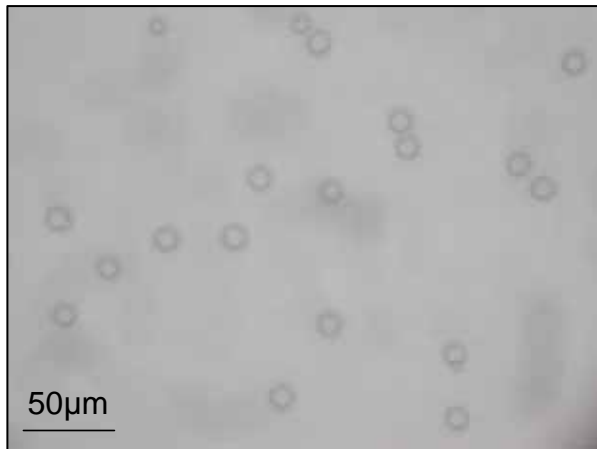
The liquid film on low-energy surface.

The liquid film is spread. (wetting)
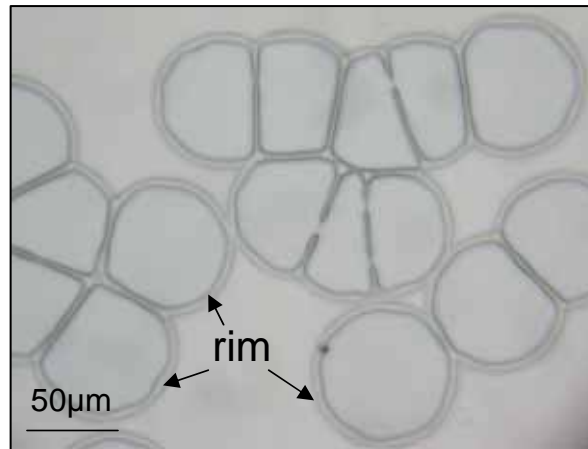
The film is broken into droplets. (dewetting)

- Dewetting通常歸類為兩種形式:
  - 洞的異質成核與成長(heterogeneous nucleation and growth)
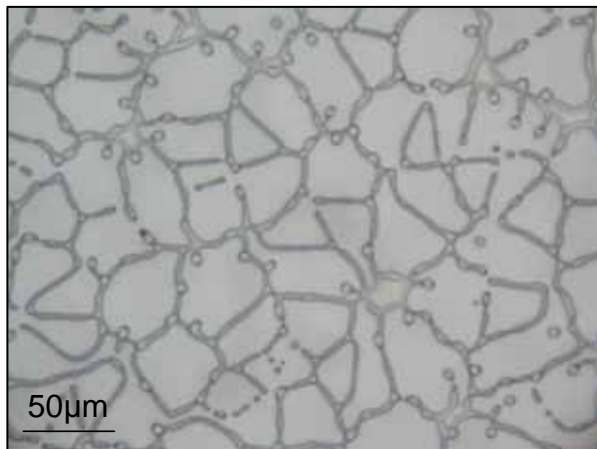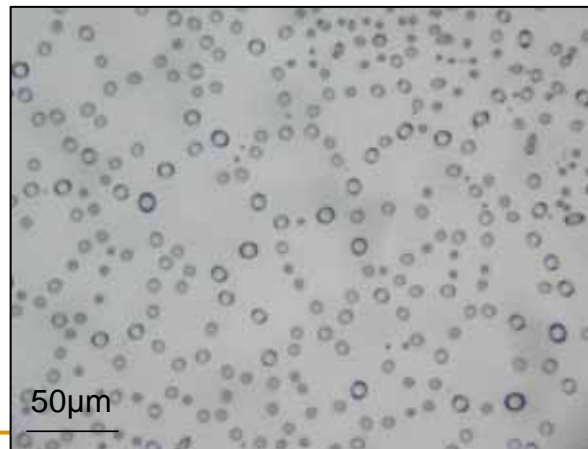 - spinodal dewetting

Nucleation-and-growth dewetting

a. 洞的成核

50μm

b. 洞的成長與接觸

rim

50μm

c. 多邊形結構

50μm

d. 形成droplets

50μm

*40nm 50k polystyrene

- 由薄膜內的 defects，像是雜質或氣泡等，引發破裂。

- 破裂之洞形成且到達基材後，因基材的表面能較低，洞的成長持續進行，以滿足降低系統之能量。

- 洞成長終致產生彼此接觸而形成 rim，之後成為多邊形網狀結構。
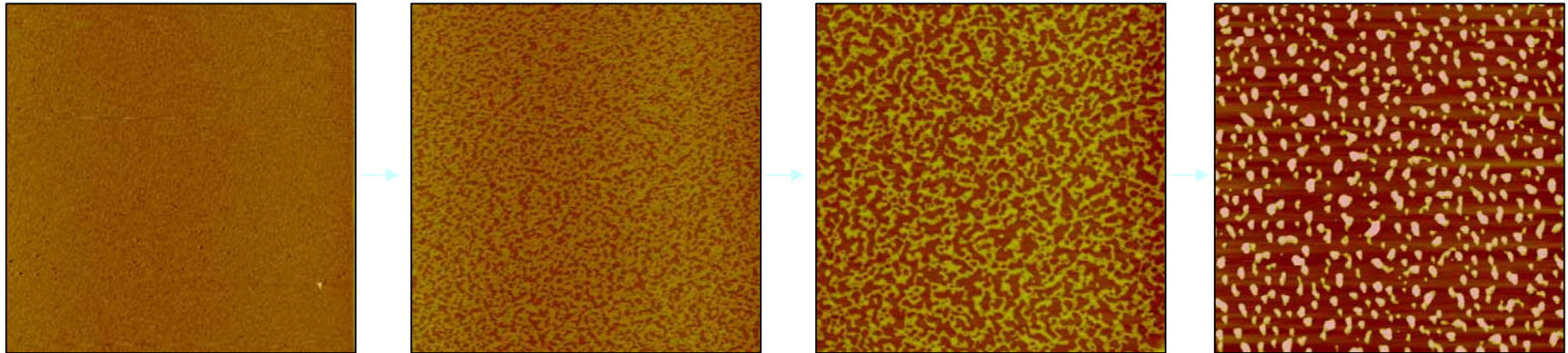
- 多邊形的邊最後由於 Rayleigh instability，分裂成像水滴狀的droplets。

- 此為異質成核與成長形式。

- Driven by stress concentration at defects.

· Incubation time.

Spinodal dewetting

- 20 μ m x 20 μ m, z range: 30nm, 10nm 13.5k polystyrene

- 型貌為兩連續相所組成的波動圖樣 兩相高度差越趨明顯，最後由高度較高的相分裂為droplets, 稱為spinodal dewetting

- No incubation time required.

- Driven by excess free energy.

- 與流體系統中，由組成擾動的spinodal decomposition很相近，惟有在薄膜系統中造成的是高度的差異(height fluctuations).
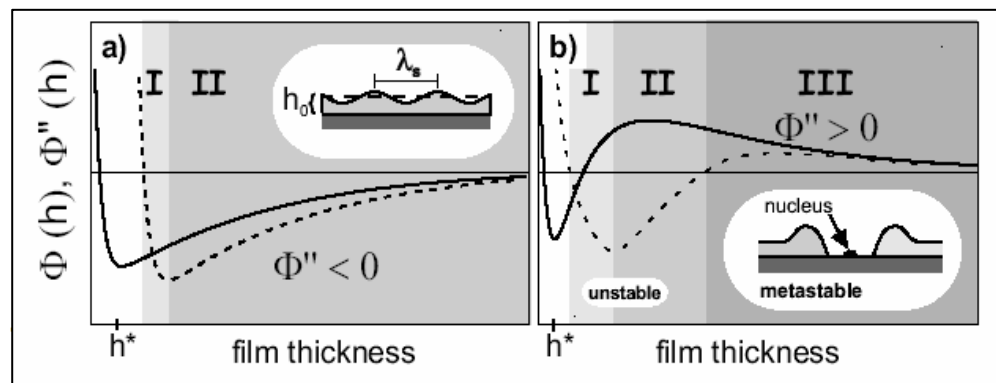
excess free energy

➢ It is used to describe the energy of a thin film system as a function of film thickness.

➢ excess free energy (Φ) is composed of long-range interactions (first term) and short-range interactions (second term). (vdW)

$$\Phi = -A/12\pi h^2 + S^P \exp(-h/l)$$

A: Hamaker constant

S^p: spreading coefficient

➢ If $\Phi'' > 0 \rightarrow$ heterogeneous nucleation (meta-stable)
    $\Phi'' < 0 \rightarrow$ spinodal dewetting (unstable)

a) I II λ_s $h_0($
$\Phi'' < 0$
$\Phi(h)$, $\Phi''(h)$
h*   film thickness

b) I II   III
$\Phi'' > 0$
nucleus
unstable   metastable
h*   film thickness

unstable system   metastable system

* Seemann, R.; Herminghaus, S.; Jacobs, K.

*J. Phys.: Condens. Matter* 2001, **13**, 4925

實驗動機及目的

• Dewetting 提供在分子尺度良好的研究平台,來研究高分子鏈在奈米薄膜中的行為,包括分子作用力,excess free energy, 基材交互作用,和分子鏈之受力鬆弛(relaxation).

•文獻中多為研究超低分子量之薄膜,因其與liquid dewetting相似,缺少對高分子量薄膜完整的現象觀察及探討,然而高分子量薄膜特有之交纏網路結構是小分子系統中所缺乏的,故我們以研究交纏分子量之上的高分子薄膜為主,由分子動力學和熱力學的觀點出發來探究其對dewetting之影響。

Part 1

Molecular recoiling force:

Polymer films on hard substrate

Sample preparation

- PS films (10 nm – 80nm, MW= 13.5k, 50k, 200k, 400k, 900k, 2M g/mol) spin coated on silicon. (M_e ~ 17.5k g/mol)

- Dried at room temperature for 2 days.

- Annealed for various periods of time in an oven at 170℃. (dewetting)

- Examined under OM and AFMs.

PS solution

10nm-40nm

wafer

Oven

170

AFM tip
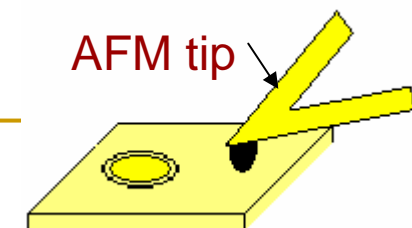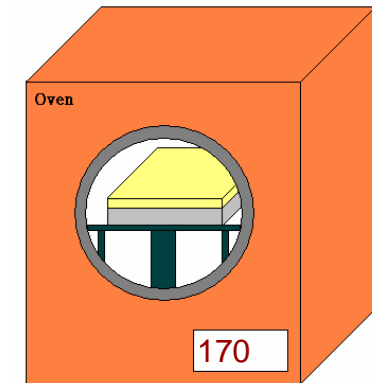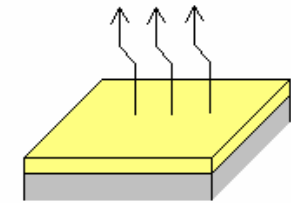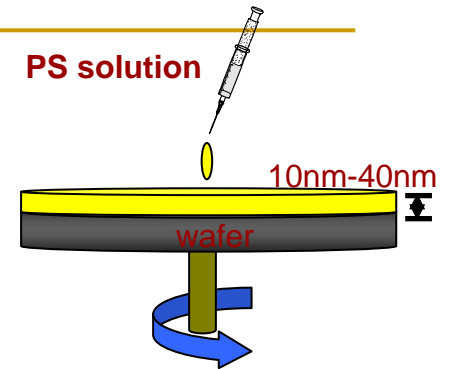
Dewetting process: PS on silicon wafer

- Nucleation of pinholes
  - Local release of the in-plane elastic stress: thickness increase at the edge: "crests"

- Film slippage along the substrate
  - After the hole touched the substrate
  - Mass pileup at the hole edge: "rim"

- Holes contacted each other and rims merged
  - to form polygon structure of "ridges"
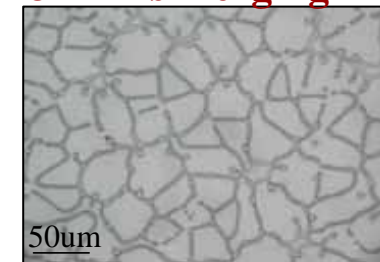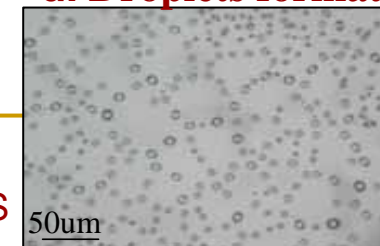
- "Ridges" shrank and droplets formed.

*40nm 50k PS

a. Nucleation of holes

crest
PS
Si
50um
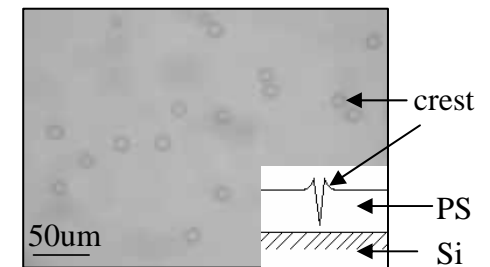
b. Holes touching substrate

Rim
50um

c. Rims merging

50um
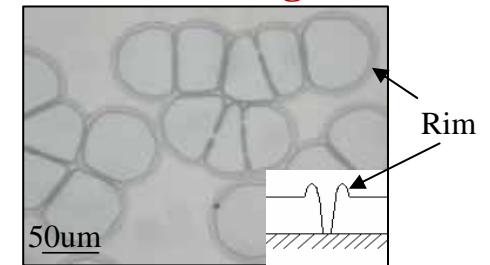
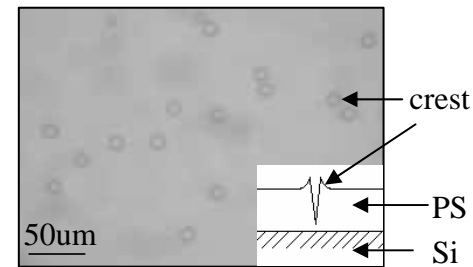**d. Droplets formation**

50um

The elastic stress release

crest

PS

Si

50um

- **Elastic stress release** due to the incipient hole nucleation and growth:
  - Least affected by the viscous process that dominates in the regime of long annealing time.

  - At the hole edge, the effect of adhesion is minimal.

  - From the maximum crest height at the hole edge, the relaxed molecular recoiling force (released stress) can be measured.
    - At least, the lower bound, considering the possible effects of chain relaxation and substrate adhesion.
    - As will be shown later, the "lower bound" values are very close to the real ones.

Calculation of the molecular recoiling force

From Hooke's law,

$$e_\gamma = \frac{1}{E}\sigma_\gamma - \frac{\upsilon}{E}(\sigma_\theta + \sigma_Z)$$

$$e_\theta = \frac{1}{E}\sigma_\theta - \frac{\upsilon}{E}(\sigma_r + \sigma_Z)$$

$$e_z = \frac{1}{E}\sigma_z - \frac{\upsilon}{E}(\sigma_\theta + \sigma_r)$$

➢ γ and   represent respectively the normal and tangential direction, z represents the thickness direction, e_{zis} is the strain in the z direction.

➢ E: Young's modulus,   : Poisson's Ratio

➢ Approximation: Simplified as a plane stress condition due to very thin film, i.e., $_z = 0$

Therefore, we have

$$e_z = -\frac{\upsilon}{E}(\sigma_\theta + \sigma_r)$$

——— eq. 1

Calculation of the molecular recoiling force－a general solution of an axially symmetric problem

Considering a thin plate with a round hole, subject to an equi-biaxial stress, p_0 , and an internal stress p_i.

➤ 2a: inner diameter of the hole; p_i: the force acting from inside the hole (for dewetting hole, $p_i=0$)

➤ 2b: the outer diameter above which the local stress perturbation due to the existence of the hole disappear. P_0 is the molecular recoiling force，
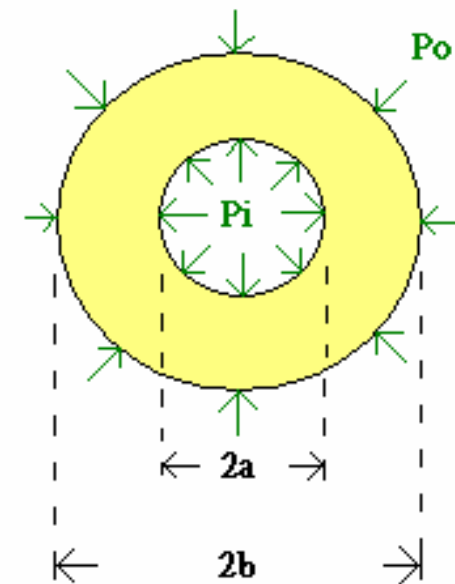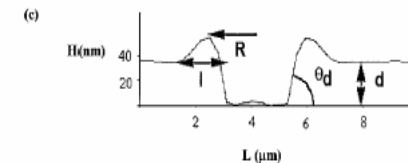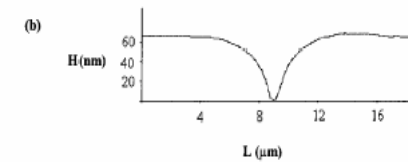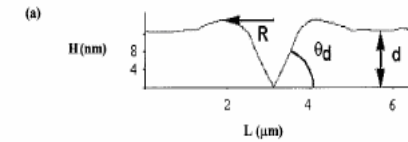
The general solution is ：

$$\sigma_\gamma = \frac{-p_0 b^2}{b^2 - a^2}\left(1 - a^2/r^2\right)$$ —— eq. 2

$$\sigma_\theta = \frac{-p_0 b^2}{b^2 - a^2}\left(1 + a^2/r^2\right)$$ —— eq. 3

* S. P. Timoshenko, and J. N. Goodier, *Theory of Elasticity*, 3rd ed., McGraw-Hill (1970)

Calculation of molecular recoiling force

Before dewetting：no hole, r=a=0,

substituting eq.2, 3 into eq.1

$$e_{z(initial)} = -\frac{\upsilon}{E}(\sigma_\theta + \sigma_r) = -\frac{\upsilon}{E}2P_0 = \frac{\tau_i - \tau_0}{\tau_0}$$

— eq. 4

◆ $_i$: film thickness measured

◆ $_0$: film thickness that corresponding to no stress.

eq.4 can be converted to $=>$

$$\tau_0 = \frac{\tau_i}{(1 + \frac{\upsilon}{E}2P_0)}$$

— eq. 5

Calculation of molecular recoiling force

At maximum crest height: maximum release of the recoiling stress (r=a)

$$e_{z(final)} = \frac{\upsilon}{E}(\sigma_\theta + \sigma_r) = \frac{\upsilon}{E} 2P_0(\frac{1}{1-(a/b)^2}) = \frac{\tau_f - \tau_i}{\tau_0}$$

eq. 6

◆ $_f$ 為 film thickness at maximum crest height

Net strain: substract eq. 4 from eq. 6 yields

$$\Delta e = e_{z(final)} - e_{z(initial)} = \frac{\tau_f - \tau_i}{\tau_0} = \frac{\delta}{\tau_0} = \frac{\upsilon}{E} 2P_0(1 - \frac{1}{1-(a/b)^2})$$

eq. 7

where   is the crest height

Calculation of molecular recoiling force

Substituting eq.5 into eq.7, we have

$$\delta=\frac{2p_0}{E}(1-\frac{1}{1-\left(a/b\right)^2}\frac{\tau_i}{1+\frac{\upsilon}{E}2p_0})$$

We have ignored the effect of adhesion which is justified as δ is measured at the edge of film where adhesion is minimal.

Measurements for molecular recoiling force

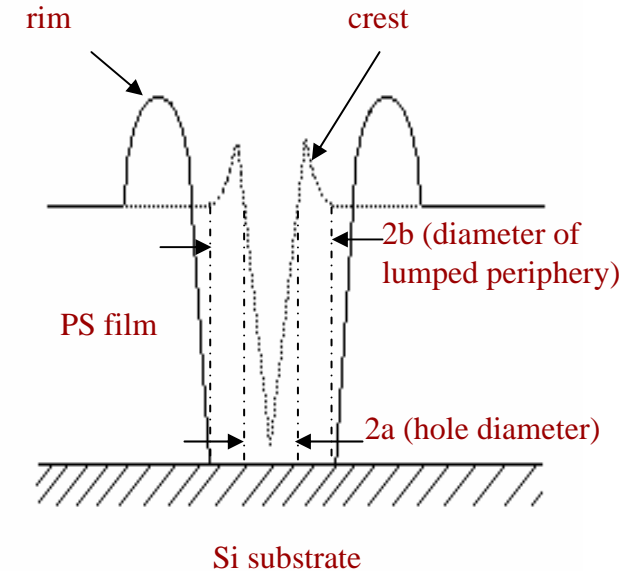- The relationship between **crest height** and p_0, the molecular recoiling stress, is*

$$\delta = \tau_f - \tau_i = (e_z - e_{z,0})\tau_0 = (e_z - \frac{2p_0\upsilon}{E})\tau_0 = \frac{2p_0}{E}\frac{(a/b)^2}{1-(a/b)^2}\frac{\tau_i}{1+\frac{2p_0\upsilon}{E}}$$

where:

$_0$: local thickness under no stress

$_i$: local thickness under initial stress p_0,

$_f$: local thickness under relaxed tension at maximum crest height

rim   crest

2b (diameter of lumped periphery)

PS film

2a (hole diameter)

Si substrate

* M. H. Yang, S. Y. Hou, Y.L. Chang, A. C.-M. Yang, PRL 2006, **96**, 066105.

Development of Crest and Rim : 200k and 400 MW

Legend:
○ □ ☆ : Crest heights
● ■ ★ : Rim heights

= 30 nm

= 40 nm

= 18 nm

(Inset axes: Height of crest or rim (nm) vs Hole diameter (nm); Height of crest or rim (nm) vs Hole depth (nm))

Main axes: Height of crests or rims (nm) vs Depth of holes (nm)
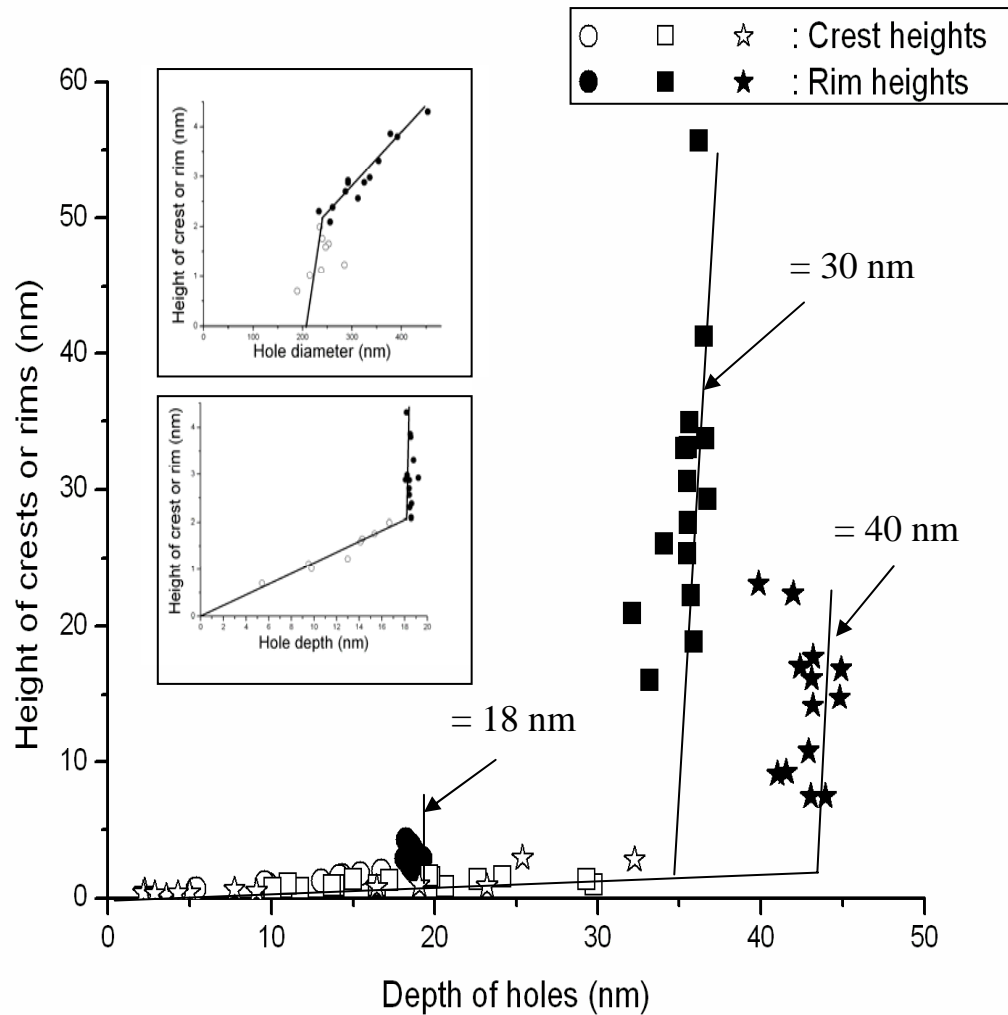
Two regimes:

Crest formation &

Rim formation.

Crest formation:

Dissipation of the molecular recoiling force

No substrate exposed.

200k PS film thicknesses: 18 nm, 30nm, and 40 nm.

Insets: (above) Crest and rim height 18 nm thickness as a function of the hole diameter; (below) The blow-up plot of the crest and rim height versus hole depth.

* M. H. Yang, S. Y. Hou, Y.L. Chang, A. C.-M. Yang, PRL 2006, **96**, 066105.

Molecular recoiling force

- The molecular recoiling forces were
  - from 8.0 to 35 mN/m.
  - Increasing with molecular weight
  - Decreasing with film thickness for the regime 10 nm $< \tau <$ 40
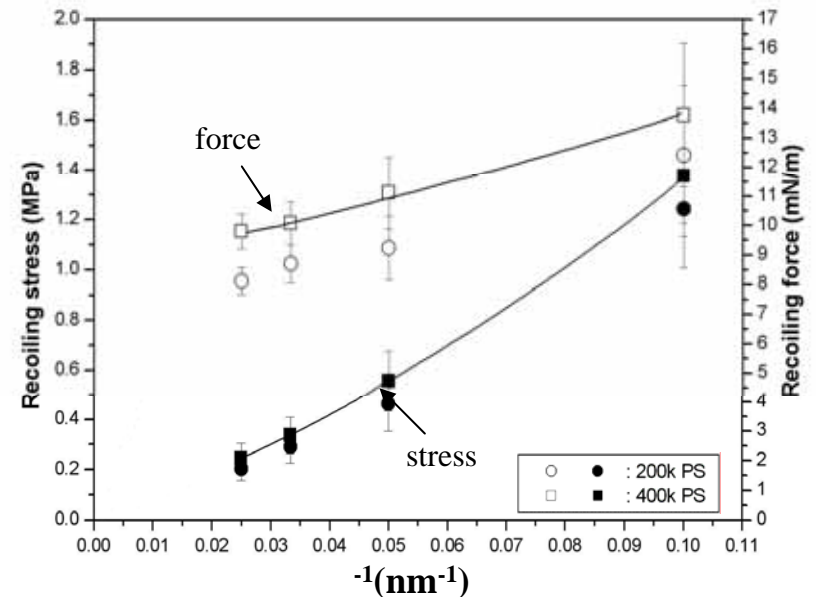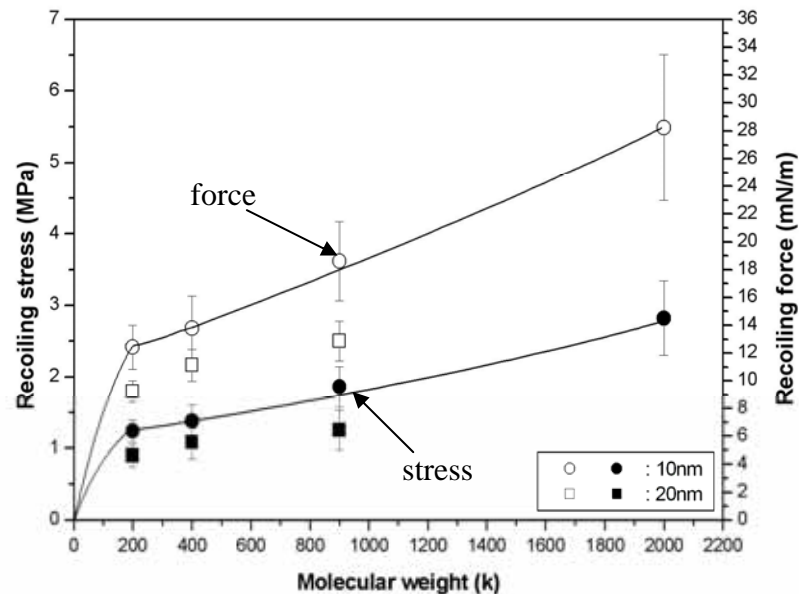
*Recoiling stresses and recoiling forces in thin PS films calculated from maximum crest heights.

* M. H. Yang, S. Y. Hou, Y.L. Chang, A. C.-M. Yang, PRL 2006, **96**, 066105.

Summary 1

- Molecular recoiling force is operative in thin polymer films, contributing to the residual stress that may cause film instability.

- This force can be measured from the incipient hole geometry.

- The recoiling stress was found to increase with molecular weight and decreasing film thickness.

Part 2

Total dewetting forces in thin film:

Polymer films on soft substrate

(unpublished results deleted)

Part 3

Excess free energy:

Effect of MRF

(unpublished results deleted)

Part 4

Luminescent enhancement by dewetting
for conjugated polymers

(unpublished results deleted)

Part 5

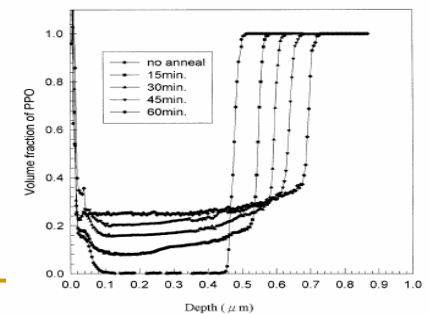## Mechanical coupling between nanofilms and substrate:
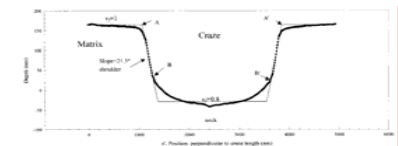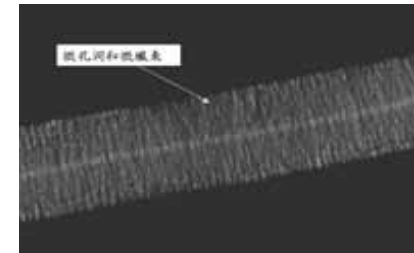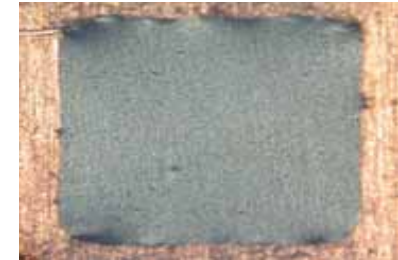
Two-stage dewetting

(unpublished results deleted)

Ramifications for future study

- Glass transition in ultrathin films
- π-π interactions for surface tension and molecular recoiling force (chain aggregation) vs. Entropy force
- Chain motion at glassy state (physical aging)
- Entanglement density for ultrathin films
- Molecular deformation during spin coating thin films
- Frictional/ sliding of polymer films on substrate
- Nano-resists
- Quantum well / quantum dot polymer LED
- Single-molecule polymer LED

奈米薄膜高分子鏈在力場的運動

- 奈米薄膜之拉伸形變與應力鬆弛-奈米尺度觀察與量測

  - 超密銅網上之自由薄膜 [9]
    - Weibull distribution prevails in fracture of polymers
  - 彈性基材上之附著薄膜

  - 以AFM 及近場光學方法,研究因形變與應力鬆弛造成的表貌(與發光行為)的變化
  - 奈米力學計算: 由AFM表貌,計算應力與應變分佈[9]

  - 彈性形變: Affine deformation
  - 非彈性形變: non-affine deformation
    - Cooperative motions of chains – Local clustering of entanglements
    - Crazing, shearing, yielding, strain hardening and softening: Nanoscale observations

- 高分子材料表面的高分子鏈,其物理現像,亦與奈米高分子薄膜相似,因為其分子鏈皆受到表面能的強烈影響.
  奈米薄膜分子鏈的界面擴散:
  - SIMS [10]
  - 分子組態對擴散的影響

C.H. Lin and A. C.-M. Yang, *Macromolecules* (2001).
H.C.Lin, I.F.Tsai, A. C.-M. Yang, M.S. Hsu, and Y.C. Ling, *Macromolecules* (2002).

奈米碳管-高分子鏈 交互作用

- 奈米碳管與高分子鏈之間的奈米機械與光電交互作用,是高分子奈米複合材料以及高性能光電材料的重要關鍵.

- 奈米碳管可藉由表面接枝聚合高分子[15]或以π-π物理吸附方法,解決分散於高分子的問題.
  - 奈米碳管表面,可接枝不同長度,不同密度,以及不同分子結構的高分子鏈[16].
  - 多壁碳管,雙壁碳管,以及單壁碳管,有非常不同的與高分子鏈機械交互作用性質.
  - 可以pyrene attachment,以物理吸附方式,改善單壁碳管在高分子內的分散性問題[17].

- 延續之前我們研究奈米碳管與高分子在薄膜微觀形變(crazing)的結果[9],我們可以繼續以奈米薄膜的除潤,分子鏈擴散,以及拉伸測試,研究奈米碳管與高分子鏈的機械交互作用.

- 將官能化的碳管加入共軛高分子中,研究其奈米薄膜在前述各種不同條件之下的光電行為,可了解激子在共軛高分子以及具有優異特性的奈米碳管複合材料內的物理行為.
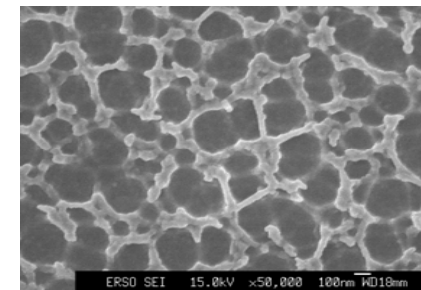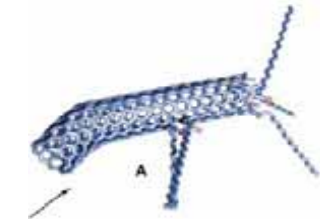
C.-C. Hsiao, T. S. Lin, L. Y. Cheng, C.-C. M. Mar, and A. C.-M. Yang, *Macromolecules* (2005).
C.W. Lin, A.C.-M. Yang, in preparation.
林敬祐, 碩士論文,清大材料系,楊長謀指導. (Manuscript in preparation).

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