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Collapse, adhesion and friction of thermoresponsive polymer brushes probed with the surface forces apparatus

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Collapse, Adhesion and Friction of Thermoresponsive Polymer Brushes

Lionel Bureau

I N S P
Institut des NanoSciences de Paris

Introduction

⇨ Design of ***smart surfaces*** and interfaces

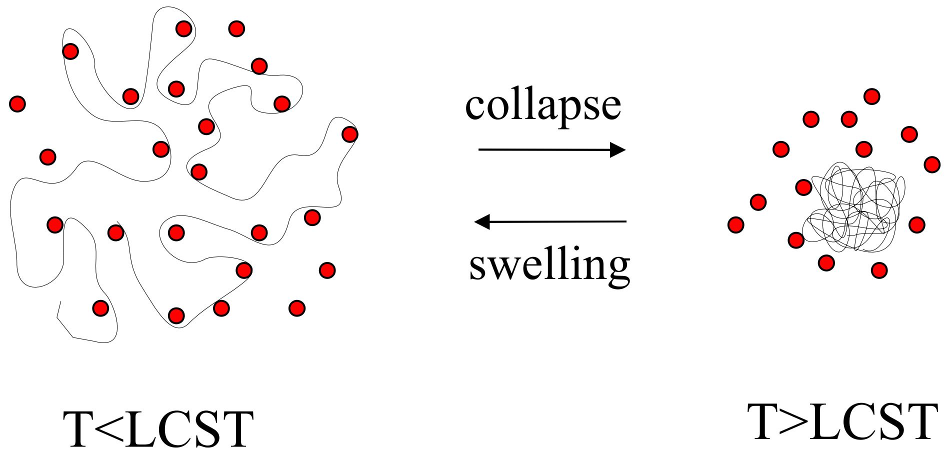
⇨ Alter wetting, adhesion or friction
with a change in environment conditions (T°, pH, ...)

⇨ Use of surface-bound ***stimuli-responsive polymers***

Introduction

⇨ Thermoresponsive polymer layers:

polymer/solvent systems with a
Lower Critical Solution Temperature (LCST)

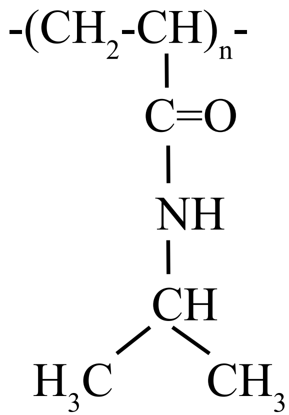


Occurs in mixtures with H-bonds between constituents

[R. E. Goldstein J. Chem. Phys. **80** (1984)]

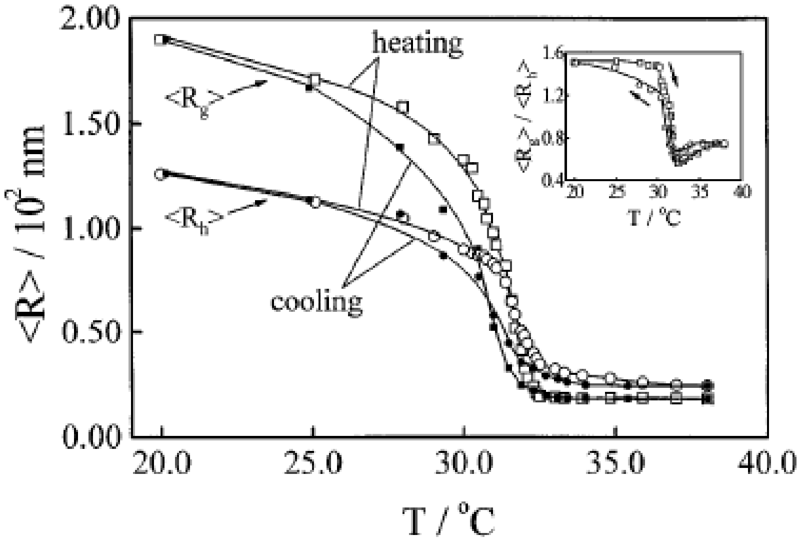
Introduction

⇨ poly(N-isopropylacrylamide): PNIPAM



T_{lcst}~32°C

Sharp coil-to-globule transition
Large change in chain size

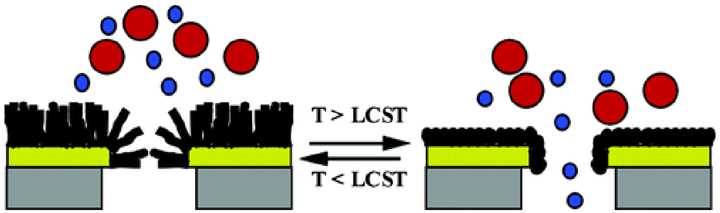


C. Wu and X. Wang, PRL **80** (1998)

Introduction

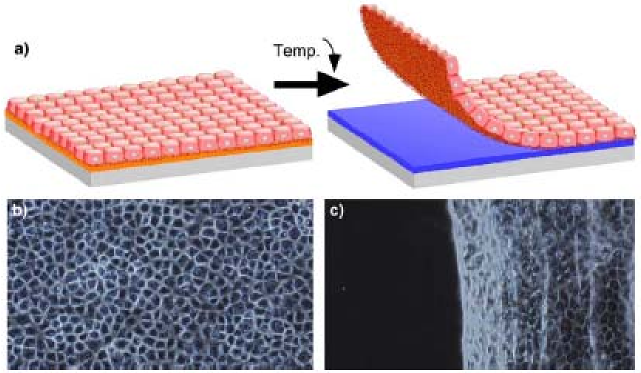
⇨ **PNIPAM grafted surfaces for:**

❶ actuation and flow control in micro/nanofluidics



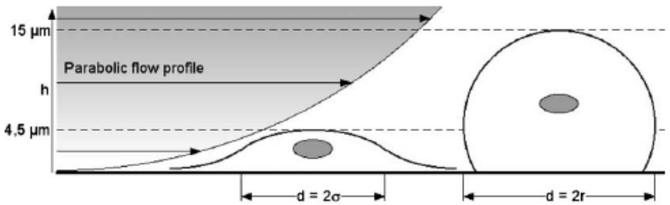
I. Lokuge *et al*. Langmuir **23** (2007)

❷ thermal switching of adhesion in bioengineering: protein sorting, harvesting of cultured cells



A. Kikuchi and T. Okano, J. Cont. Rel. **101** (2005)

❸ cell detachment in microfluidics...



O. Ernst *et al*. Lab Chip **7** (2007)

Introduction

⇨ ***Questions:***

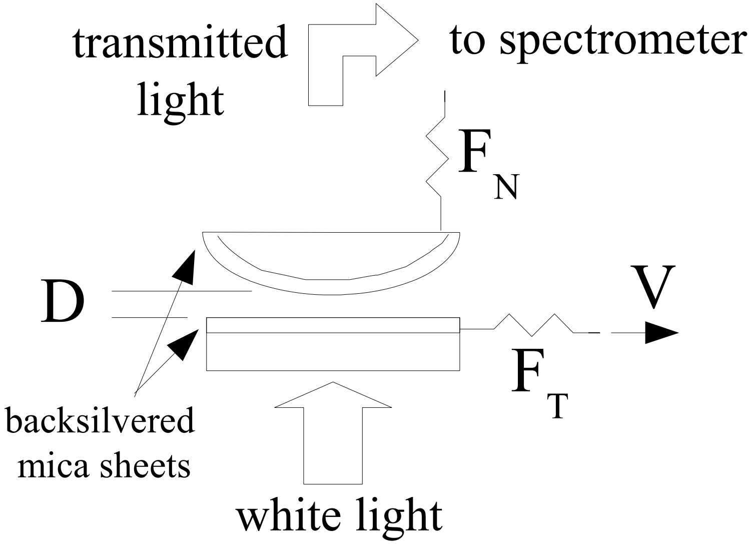
❶ effect of chain tethering on coil-globule transition ?

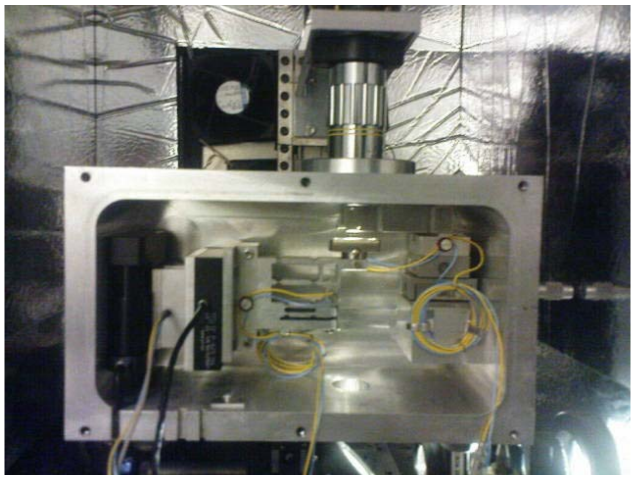
❷ influence of molecular structure on the properties of thermoresponsive layers ?

⇨ ***Probe the collapse of PNIPAM brushes with the SFA****

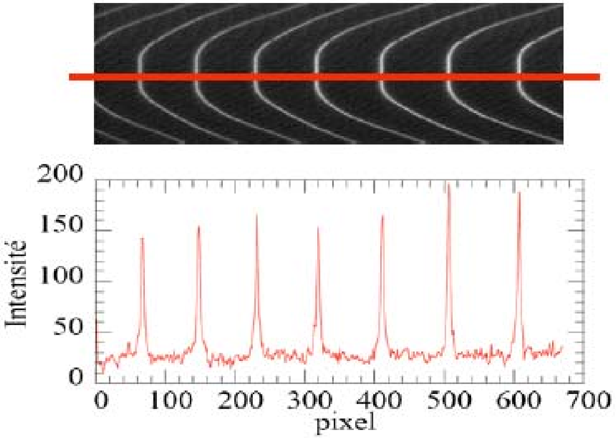
* D. Leckband *et al.*, Langmuir **23** (2007) – **22** (2006)
I. B. Malham and L. Bureau, submitted to Langmuir (2009), preprint http://fr.arxiv.org/abs/0909.3709

Surface Forces Apparatus





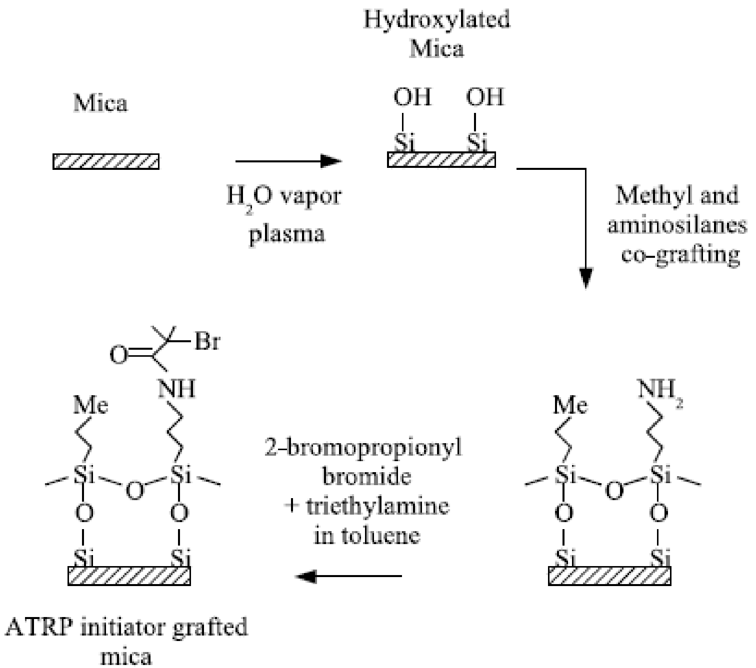
L. Bureau, Rev. Sci. Instrum. **78** (2007)

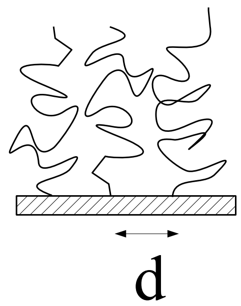


- D measured by MBI @ 30Hz
- F_N measured independently of D
- Shear amplitude up to 500 µm
- Feedback on F_N or D while shearing

Surface Chemistry

Parker et al. J. Phys. Chem. **93** (1989)





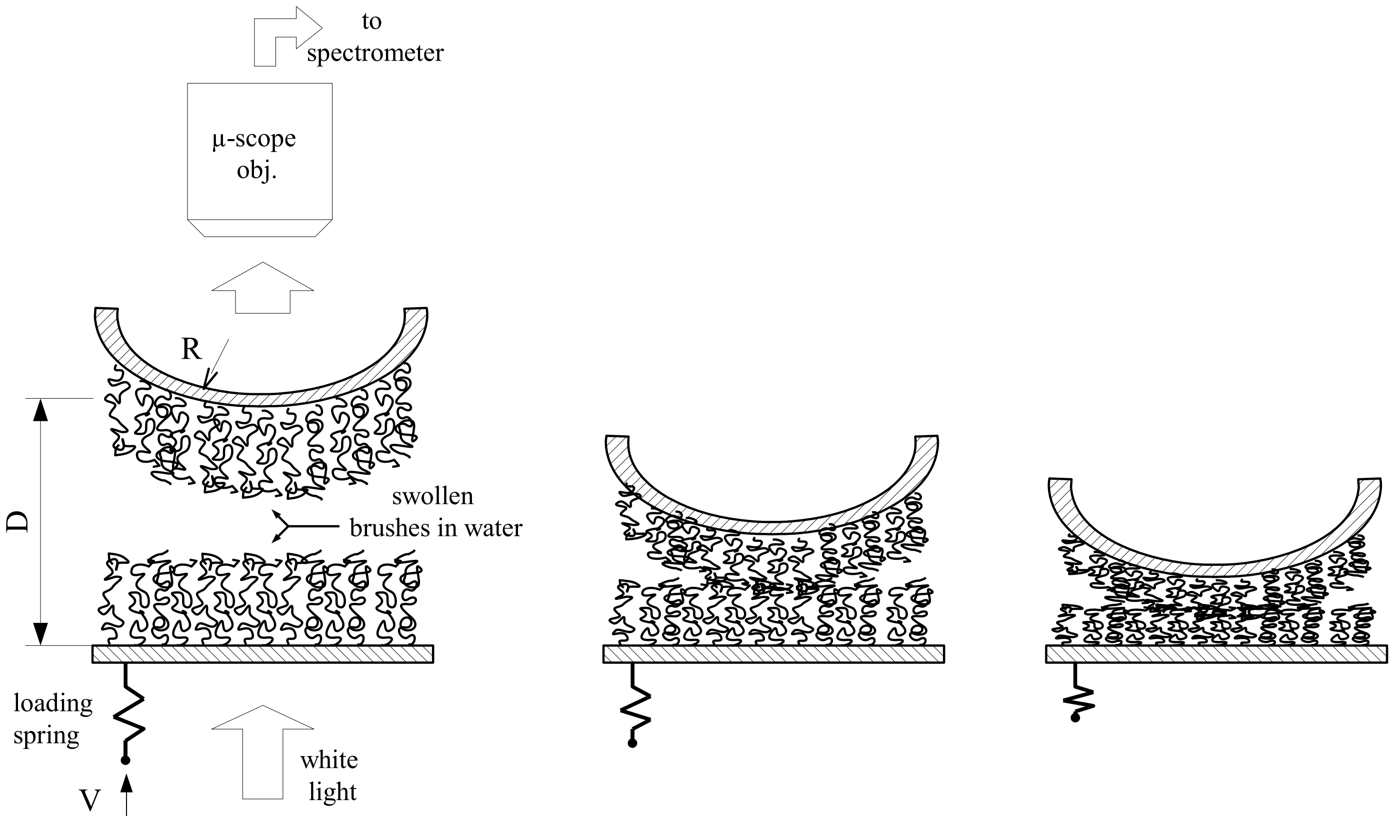
ATRP intiator grafting + brush growth

Control parameter: grafting density ($1/d^2$)

$6 \leq R_F/d \leq 30$

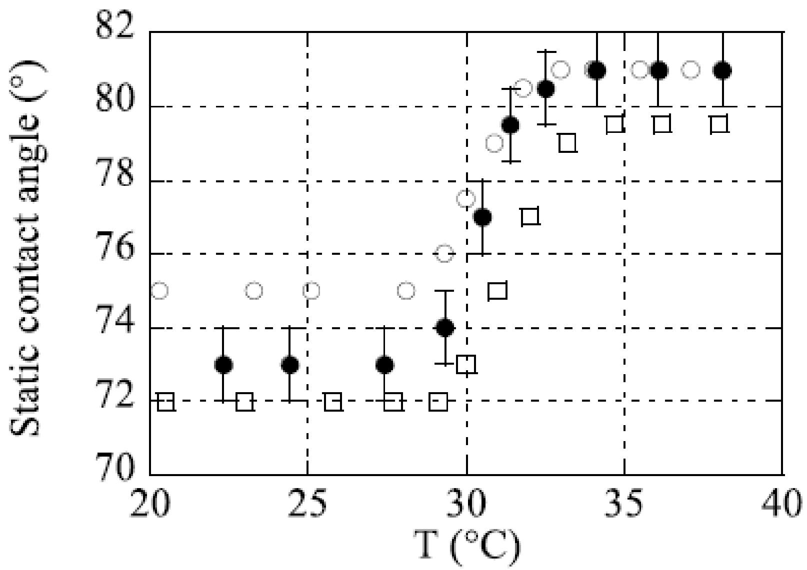
⇨ Stretched chains

Experimental configuration



Compression/adhesion of two identical brushes as a function of temperature

Temperature-dependent wetting



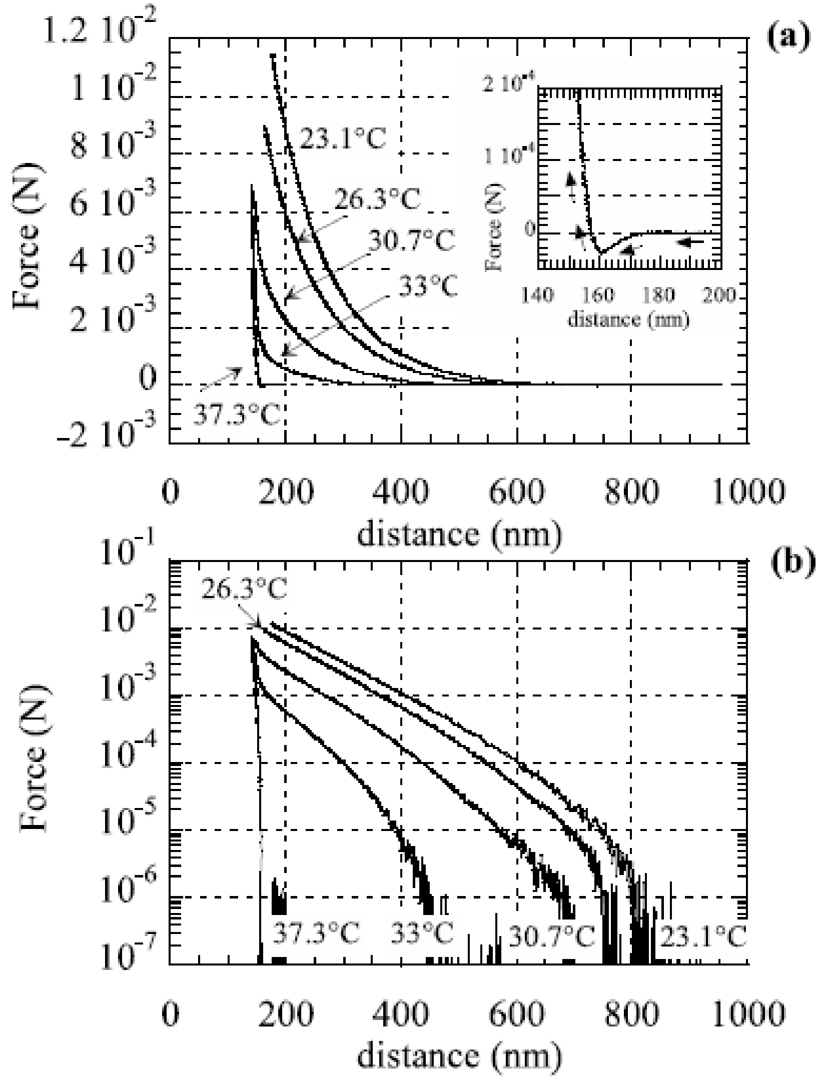
(□) 0.02 ch/nm² - (•) 0.24 ch/nm² - (o) 0.42 ch/nm²

❶ Increase in water contact angle between 30-34°C

❷ Weak sensitivity to grafting density

⇨ Outermost region of brushes exposes CH_3 groups at high T°

Compression



❶ Range of repulsive forces ↘ when T ↗

⇨ ***collapse of brushes***

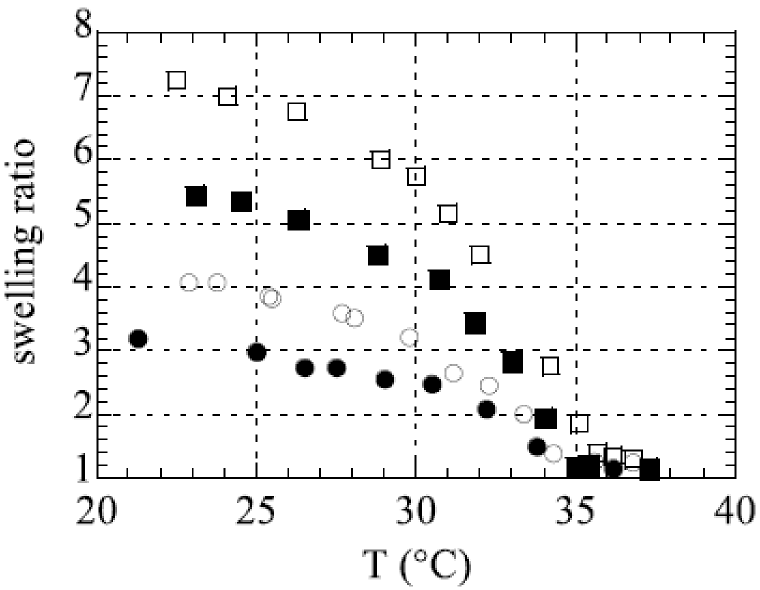
❷ At T>34°C:

attractive interaction upon approach

⇨ ***hydrophobic forces ?***

Density-dependent collapse

Swelling ratio:
$\alpha = h_{swell}/h_{dry}$



(□) 0.02 ch/nm² - (■) 0.14 ch/nm² - (o) 0.24 ch/nm² - (•) 0.42 ch/nm²

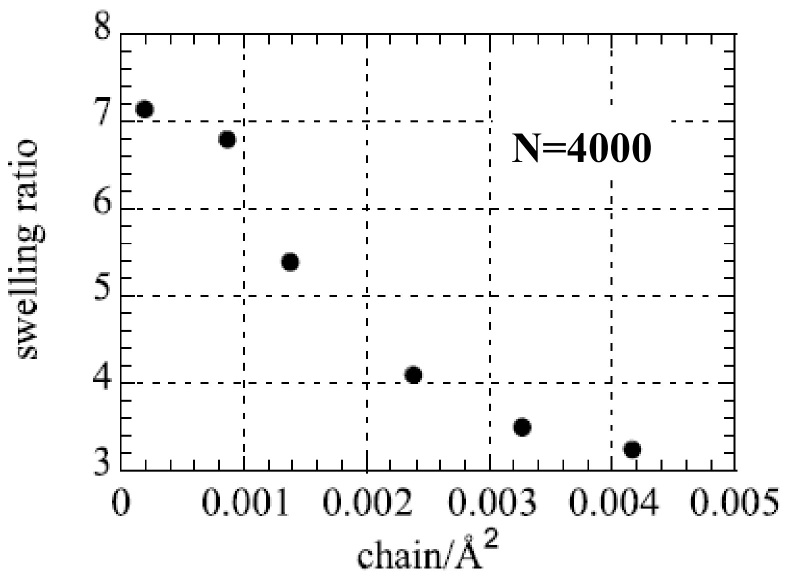
➊ **Collapse of grafted chains broader than free dilute chains**

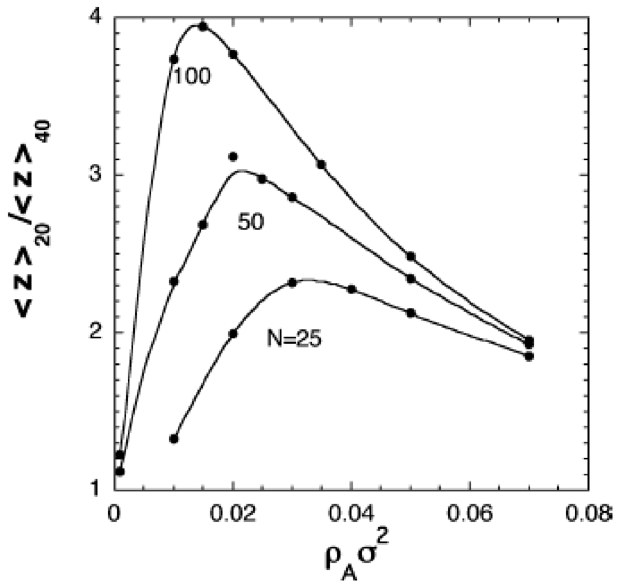
⇨ Agreement with Neutron Reflectivity results [Yim *et al*, Macromolecules **39** (2006)]

⇨ Ok with theory by Zhulina et al.[Macromolecules **24** (1991)]

Density-dependent collapse

❷ **Less dense brushes swell more**



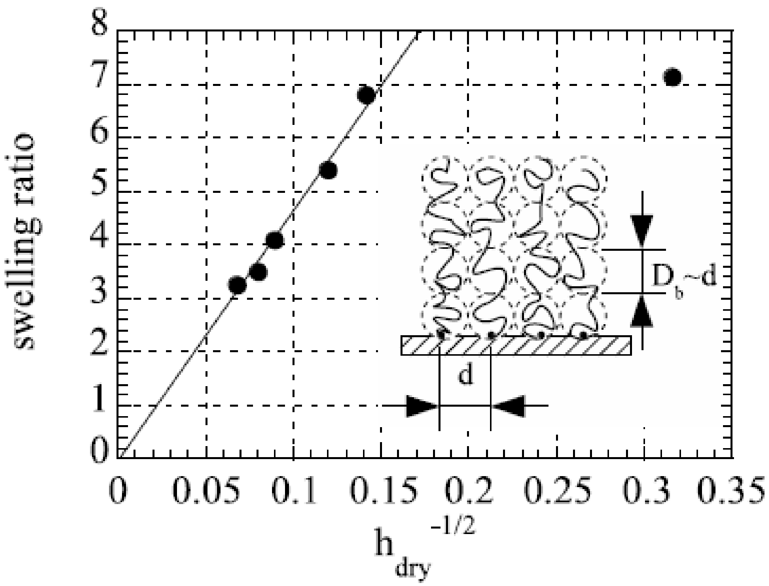


⇨ Qualitative agreement with SCF calculations

[Mendez et al. Macromolecules **38** (2005)]

Density-dependent collapse

Alexander-de Gennes scaling ?



$D_b = g^{\nu} a$ ν=3/5 for semi-dilute blobs

$$h_{\mathrm{swell}} = Na \left(\frac{d}{a}\right)^{1-1/\nu}$$

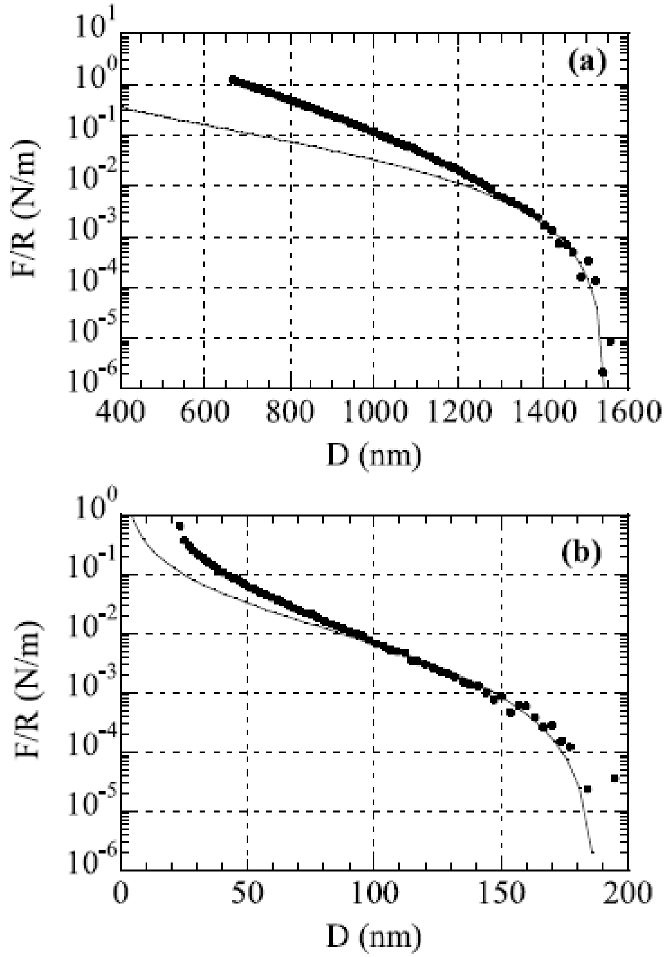
$$h_{\mathrm{dry}} d^2 = Na^3$$

$$\alpha = \frac{h_{\mathrm{swell}}}{h_{\mathrm{dry}}} = \left(\frac{d}{a}\right)^{3-1/\nu}$$

ν≈1/2 ⇨ ***validity of semi-dilute assumption ?***

… already observed for dense brushes [S. Yamamoto *et al.*, Macromolecules **33** (2000)]

Repulsive forces



Alexander-de Gennes prediction for brush compression:

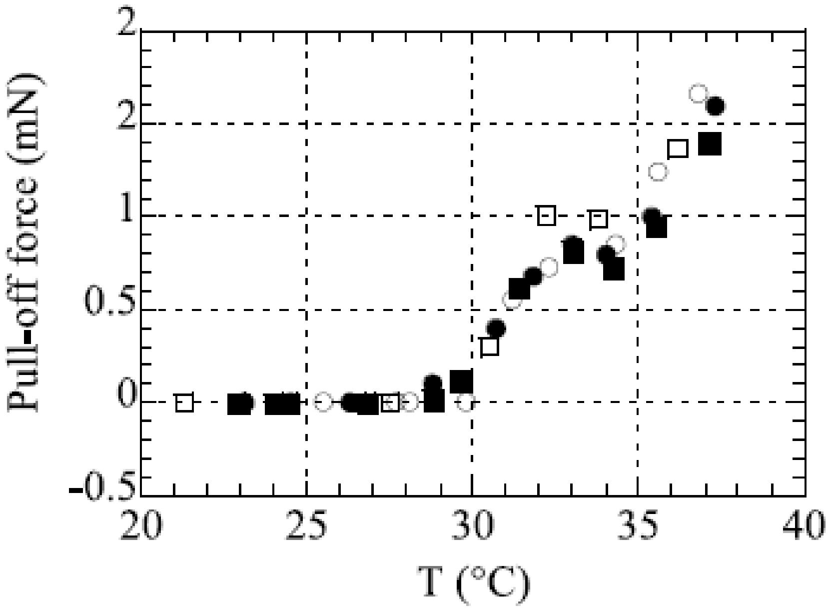
$$\frac{F(D)}{R} = C\left[7\left(\frac{D}{2L}\right)^{-5/4} + 5\left(\frac{D}{2L}\right)^{7/4} - 12\right]$$

Ok at low brush compressions, but...

Poor description under strong compression

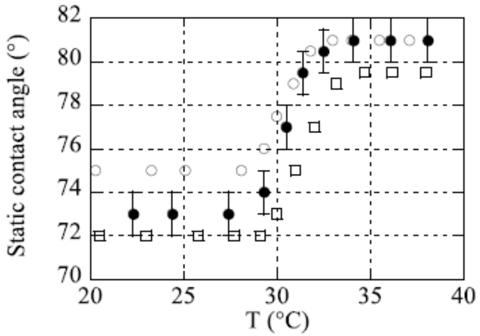
⇨ semi-dilute assumption breaks down when the monomer volume fraction is ≥ 0.3

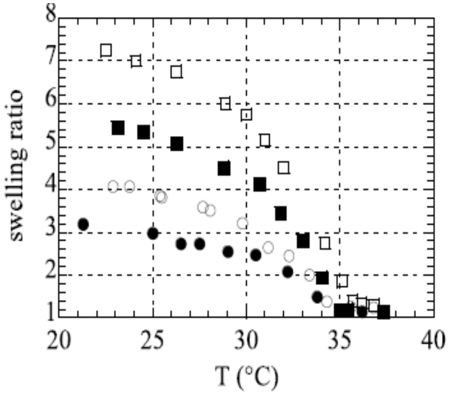
Adhesion

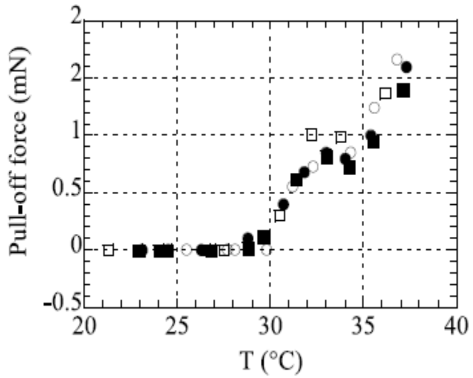


Pull-off force insensitive to grafting density

Adhesion







Adhesion increases above 35°C whereas contact angle plateaus...

❶ Brush collapse accompanied by exposure of $-CH_3$ at the polymer/water interface

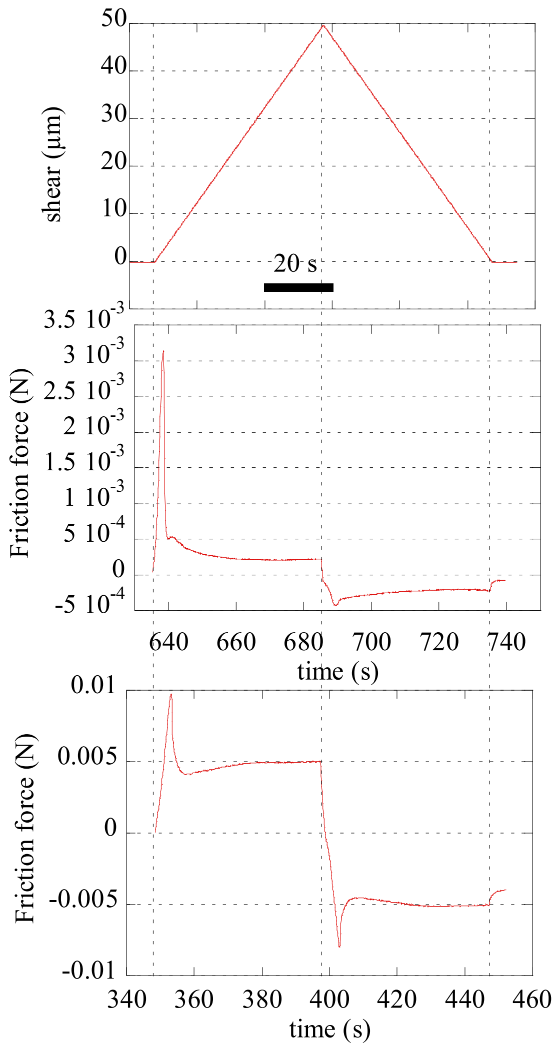
But...

❷ Another mechanism at play for adhesion:

H-bonds formation ?

Friction

$F_N = 3.10^{-3}$ N



T=26°C: **$F_{steady} = 2.10^{-4}$ N**

T=35°C: **$F_{steady} = 5.10^{-3}$ N**

Conclusions

➊Dense polymer brushes probed with the SFA

➋Extensive study of the collapse of thermosensitive brushes
⇨Test of polymer brush theories

➌Intriguing temperature dependence of brush/brush adhesion
⇨Role in bioadhesion ?

➍Huge effect of temperature on PNIPAM friction