Utilising Scattering Techniques For Investigating Polymers Under Confinement

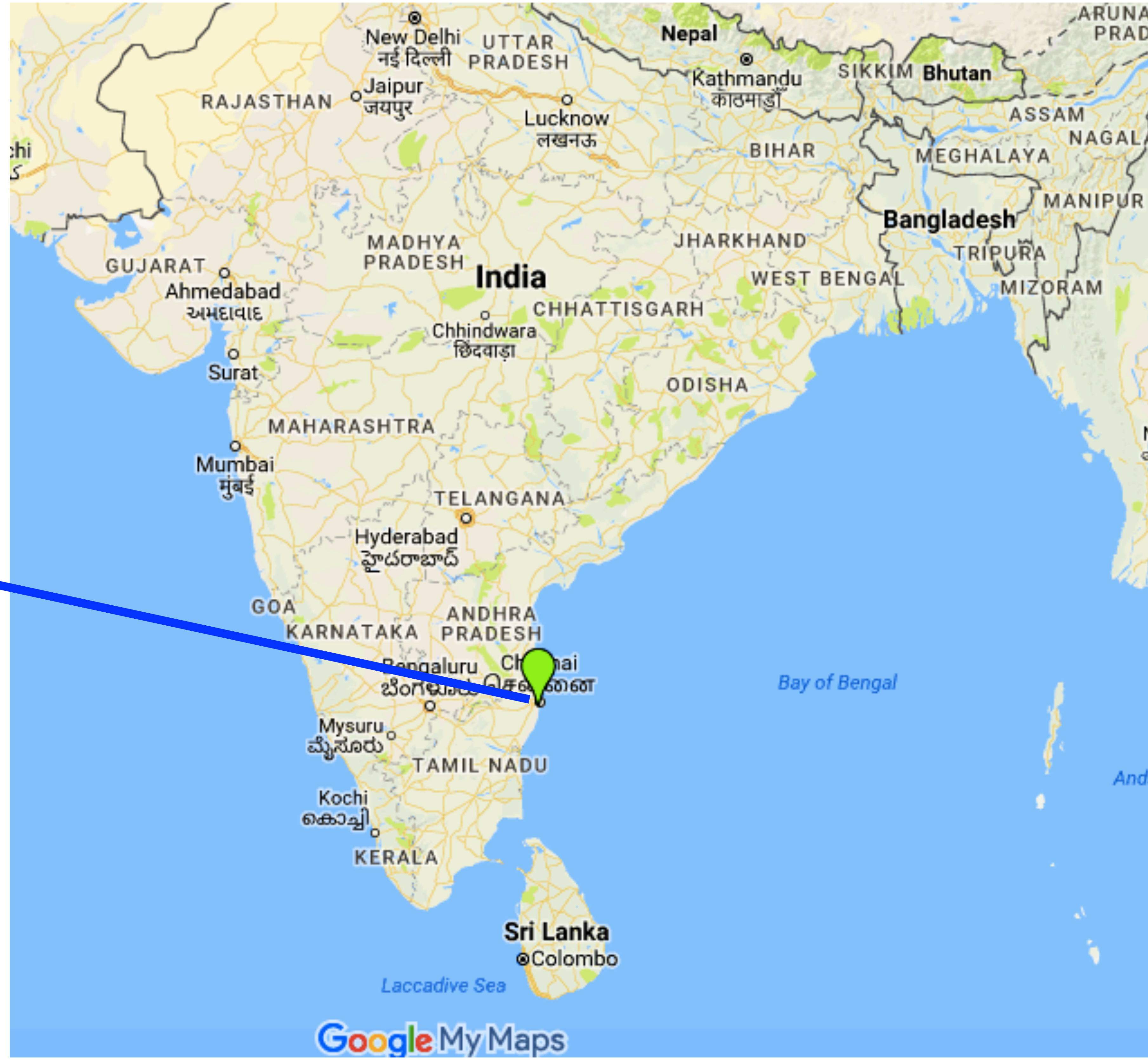
Dillip K. Satapathy

Soft Materials Lab, Department of Physics
IIT Madras

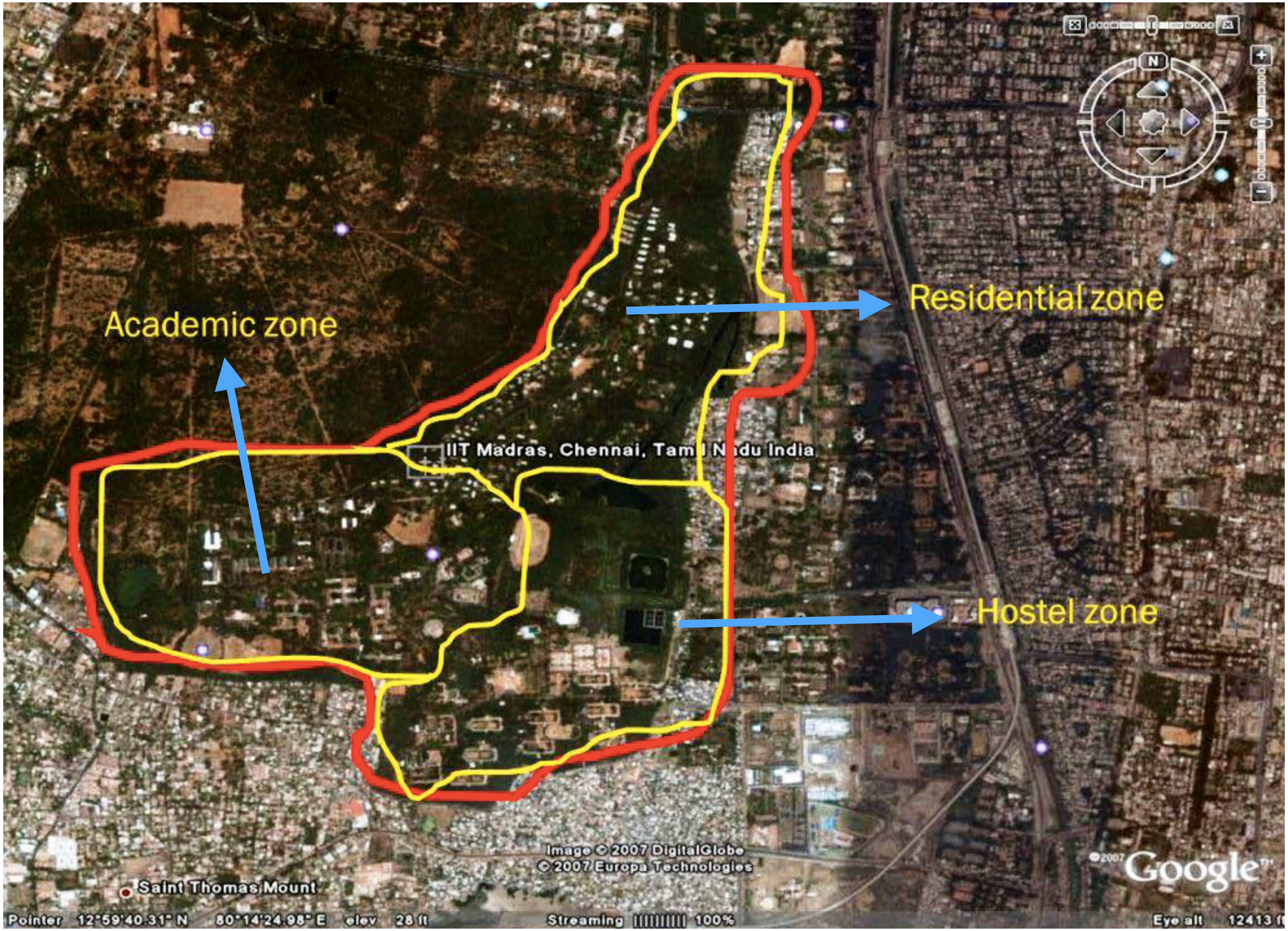
India-JNR Workshop, 18th OCT 2023

Norwegian Sea
Sweden
Finland
Norway
Russia
Denmark
United Kingdom
Belarus
Poland
Germany
Ukraine
Austria
Kazakhstan
France
Romania
Mongolia
Italy
Uzbekistan
Kyrgyzstan
Spain
Greece
Turkey
Turkmenistan
Sea of J
South Korea
China
Syria
Tunisia
Afghanistan
Iraq
Iran
East China Sea
Pakistan
Algeria
Libya
Egypt
Nepal
Saudi Arabia
India
Myanmar (Burma)
Oman
Philippine
Mali
Niger
Sudan
Thailand
Chad
Yemen
South China Sea
Burkina Faso
Gulf of Aden
Arabian Sea
Bay of Bengal
Vietnam
Philippines
Nigeria
Gulf of Thailand
Ghana
South Sudan
Ethiopia
Laccadive Sea
Malaysia
Gulf of Guinea
Somalia
Kenya
Gabon
DRC
Indonesia
Banda Sea

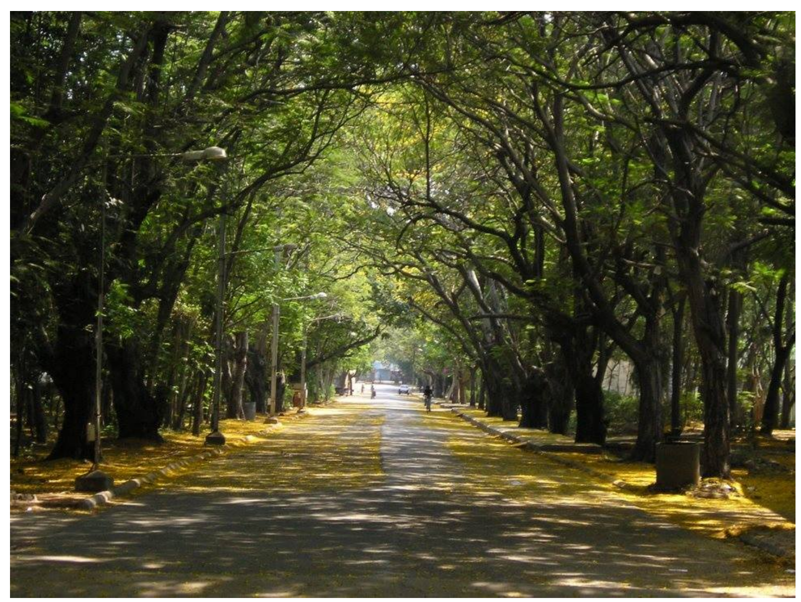
Located at Chennai, Southern India



Location, IIT Madras



Welcome to IIT, Madras



About **12,000** students; fully **residential** campus

17 departments comprising of sciences and engineering

Research Overview @ Soft Materials Lab

Polymers

- Novel properties of polymer in confinement
- Polymer membranes as actuators and sensors

Colloids

- Interface-assisted self-assembly of soft colloids and associated colloids
- Desiccation cracks under external fields

Polymers + Colloids

- Polymer based flexible thermoelectrics (polymer blends / composites)

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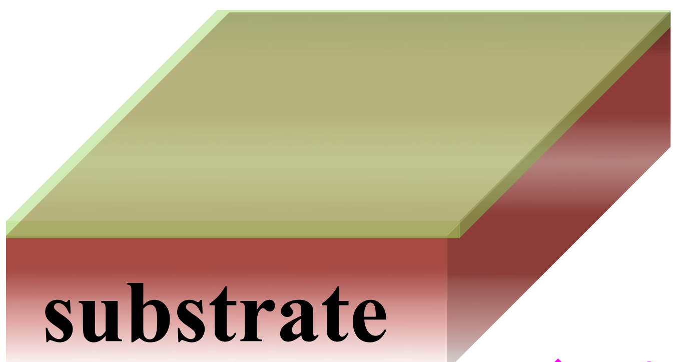
Soft Materials Lab Members

Soft Materials Lab Members

Confined Polymers

L. Pradipkanti

Polymer thin films (1-D confinement)



❖ **Finite size effects**
❖ **Interfacial effects**

- Occurrence of double glass transition temperature in aged polymer films
- Effect of polydispersity in Tg
- Densification upon confinement

L. Pradipkanti M. Choudhury, DKS, PCCP **19,** 29263 (2017)
L. Pradipkanti, DK Satapathy Thin Solid films **651,** 018 (2018)
L. Pradipkanti, DK Satapathy AIP Conf. Proc. **1832** 040029(2017)

Confined Polymers

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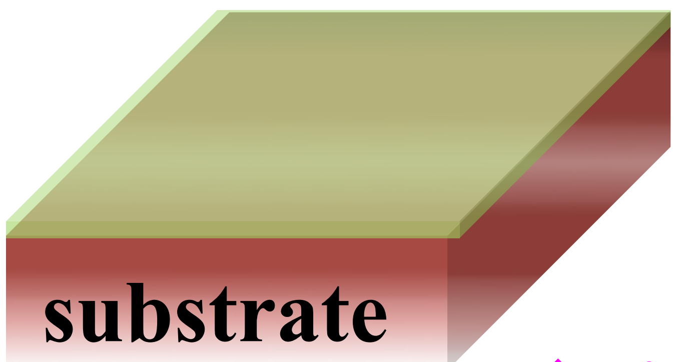

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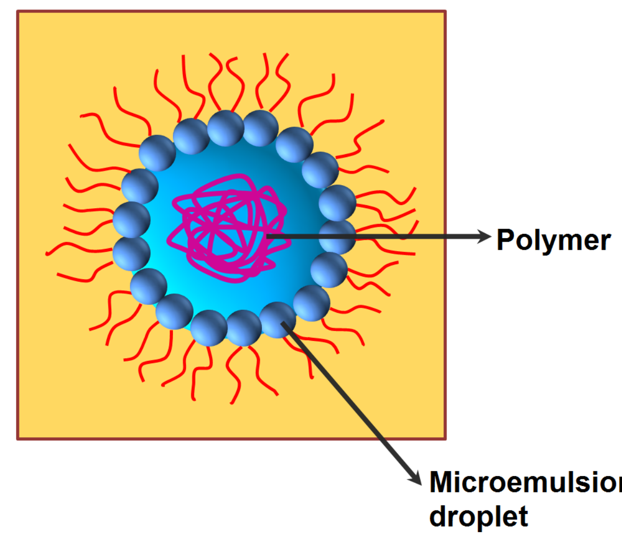
PM Geethu

Polymers under soft confinement

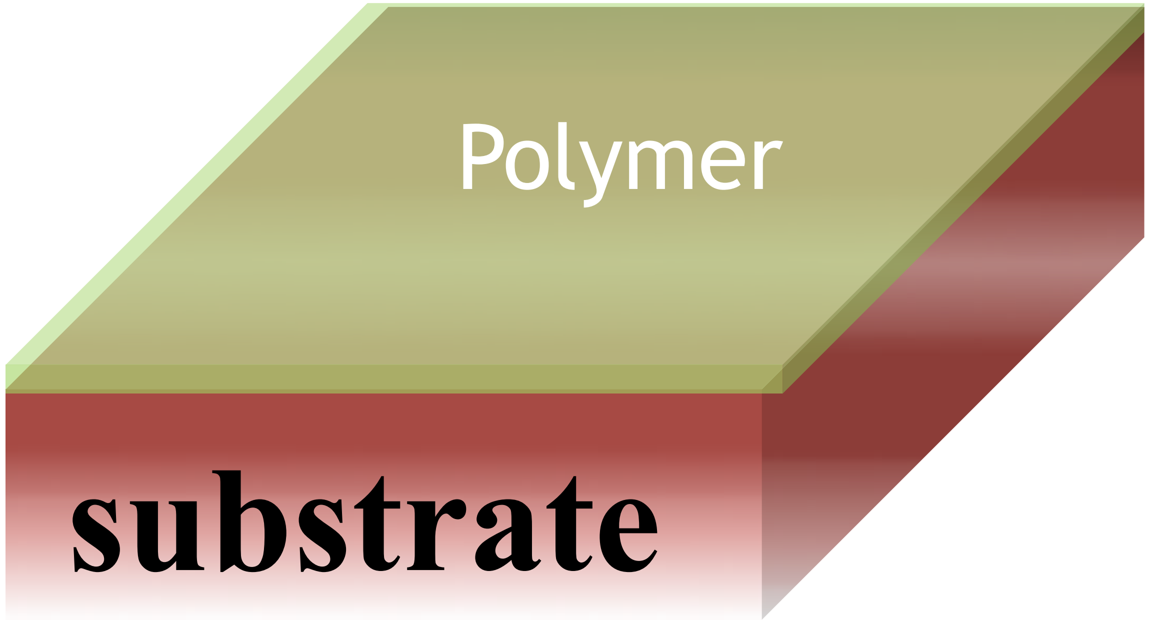


Dielectric relaxation spectroscopy
+
small angle neutron scatterng

- Enhanced dynamics of polymers

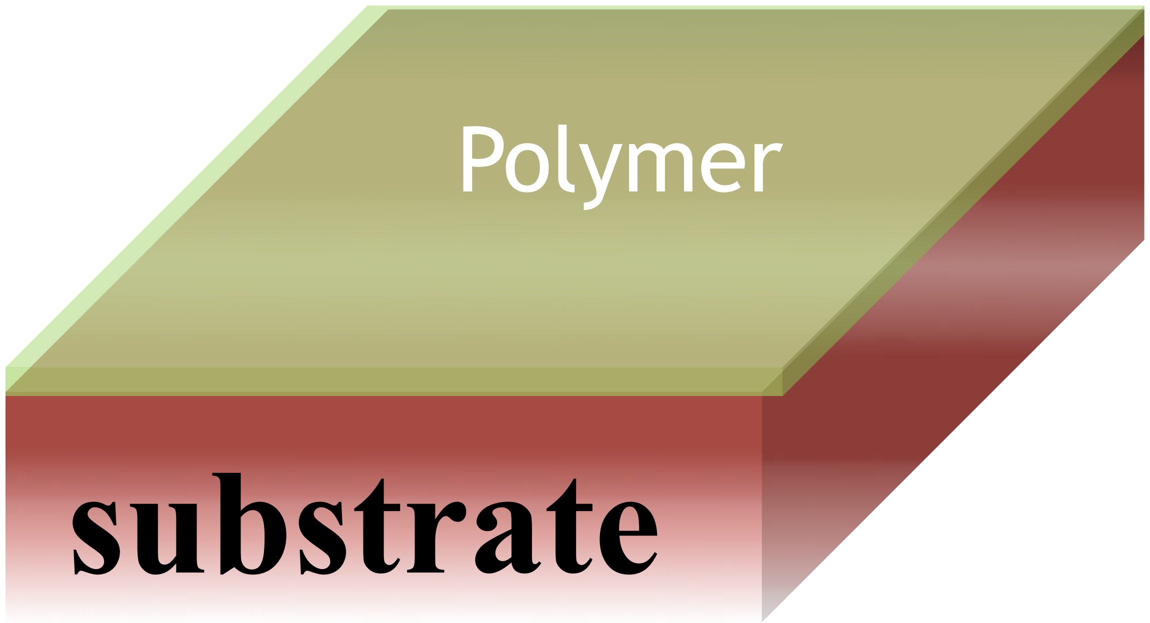
PM Geethu, I Yadav, VK Aswal DKS Macromolecules, (2018)

Confined Polymer



- The physical properties of the polymer confined to nanoscale are very different than those of the bulk
- Nanoscale confinement: thickness in the range of a few 10s of nanometers

Confined Polymer



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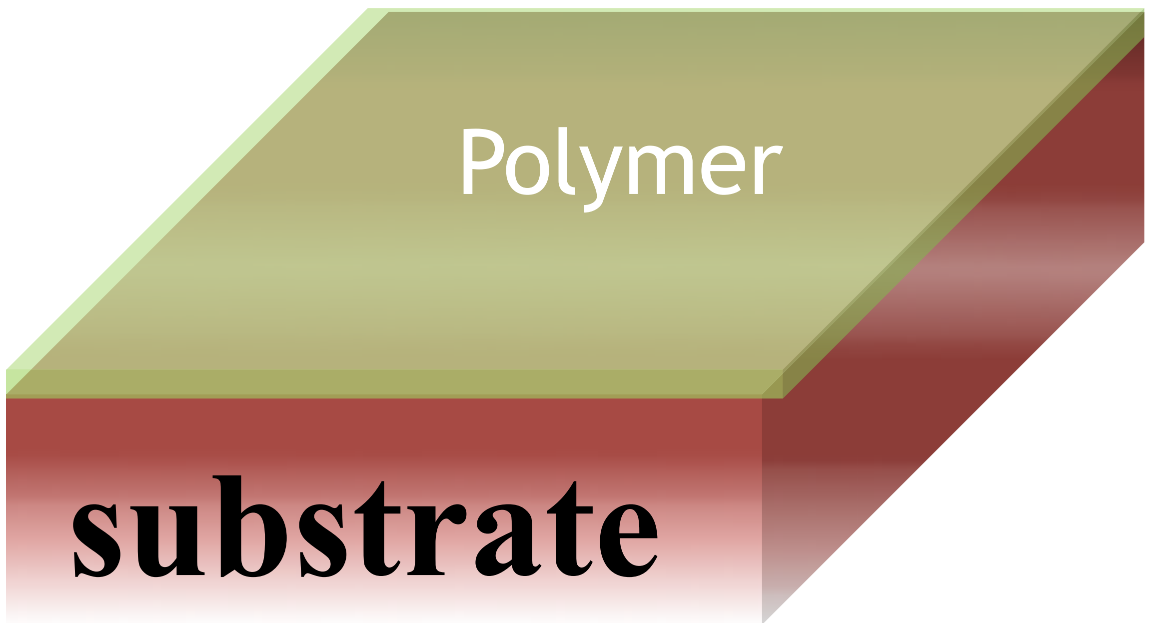
Interface play an important role in modifying the properties

Close to the confining surface the conformation of polymer chain is significantly restricted.

Confined Polymer



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PRL **110**, 108303 (2013) PHYSICAL REVIEW LETTERS week ending 8 MARCH 2013

Effect of Nanoconfinement on Polymer Dynamics: Surface Layers and Interphases

M. Krutyeva,[1] A. Wischnewski,[1] M. Monkenbusch,[1] L. Willner,[1] J. Maiz,[2] C. Mijangos,[2]
A. Arbe,[3] J. Colmenero,[3,4] A. Radulescu,[5] O. Holderer,[5] M. Ohl,[6] and D. Richter[1]

PHYSICAL REVIEW LETTERS **122**, 217801 (2019)

Effect of Local Chain Conformation in Adsorbed Nanolayers on Confined Polymer Molecular Mobility

Biao Zuo,[1,2,‡] Hao Zhou,[1] Mary J. B. Davis,[2] Xinping Wang,[1,*] and Rodney D. Priestley

PHYSICAL REVIEW LETTERS **124**, 027802 (2020)

Editors' Suggestion

Substrate Roughness Speeds Up Segmental Dynamics of Thin Polymer Films

Soft Matter

ROYAL SOCIETY OF CHEMISTRY

REVIEW

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Cite this: *Soft Matter*, 2020, **16**, 5348

Irreversible adsorption of polymer melts and nanoconfinement effects

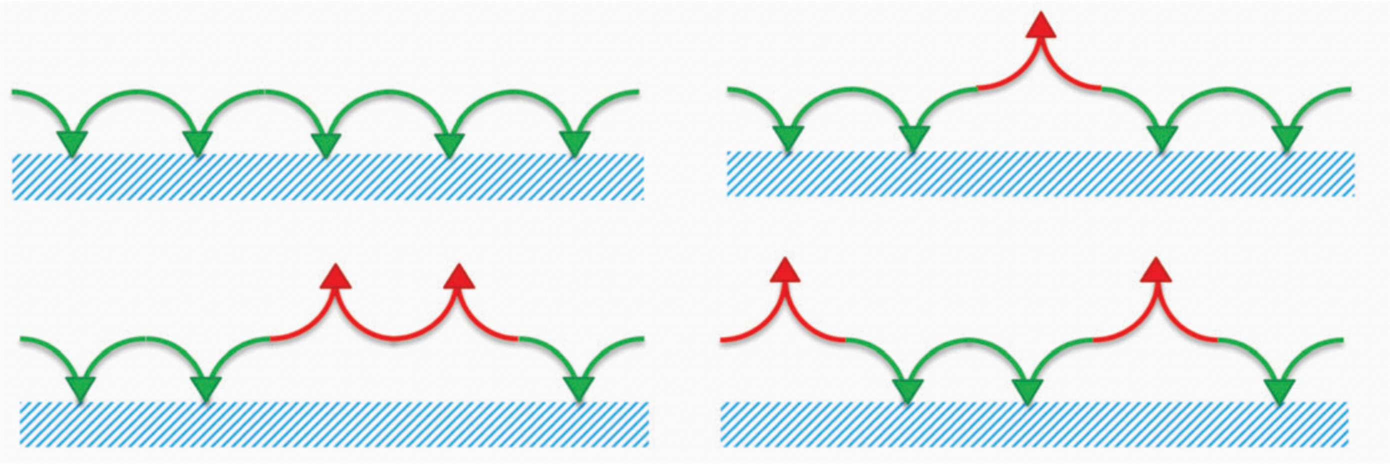
Simone Napolitano

For almost a decade, growing experimental evidence has revealed a strong correlation between the properties of nanoconfined polymers and the number of chains irreversibly adsorbed onto nonrepulsive interfaces, *e.g.* the supporting substrate of thin polymer coatings, or nanofillers dispersed in polymer melts. Based on such a correlation, it has already been possible to tailor structural and dynamics properties – such as the glass transition temperature, the crystallization rate, the thermal expansion coefficients, the viscosity and the wettability – of nanomaterials by controlling the adsorption kinetics. This evidence indicates that irreversible adsorption affects nanoconfinement effects. More recently, also the opposite phenomenon was experimentally observed: nano-

Laboratory of Polymer and Soft Matter Dynamics, Experimental Soft Matter and Thermal Physics (EST), Faculté des Sciences, Université libre de Bruxelles (ULB),

Irreversible adsorption

The adsorption of polymers can be irreversible even if the monomer substrate interaction is smaller than $K_B T$



Soft Matter, 2020, **16**, 5348–5365

Irreversible adsorption

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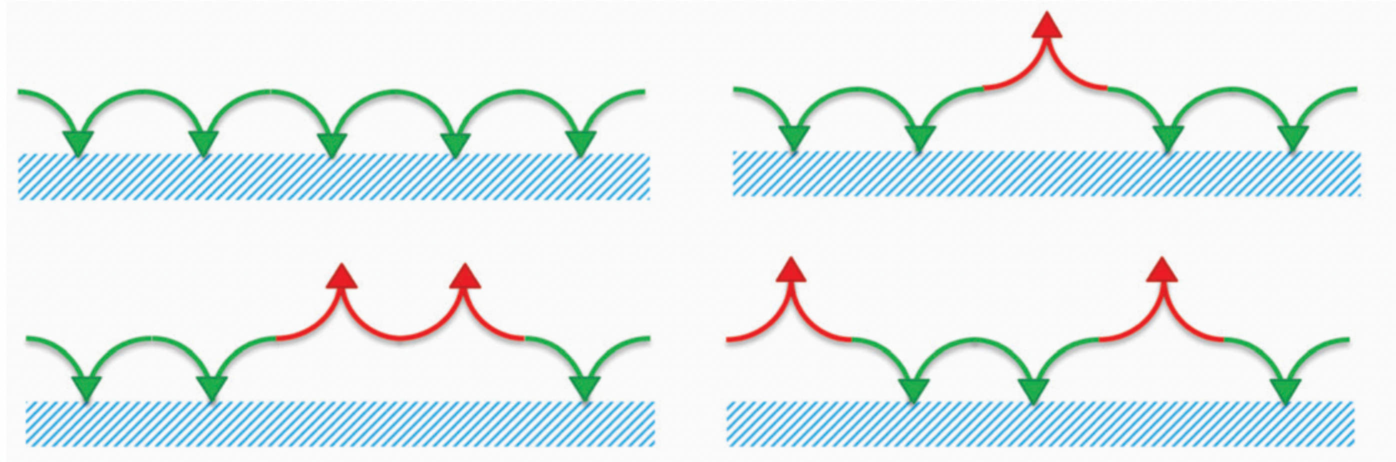

Although monomers could reversibly adsorb and desorb, the probability that the whole set of monomers (the entire chain) desorb at the same time is extremely low.

Soft Matter, 2020, **16**, 5348–5365

Irreversible adsorption

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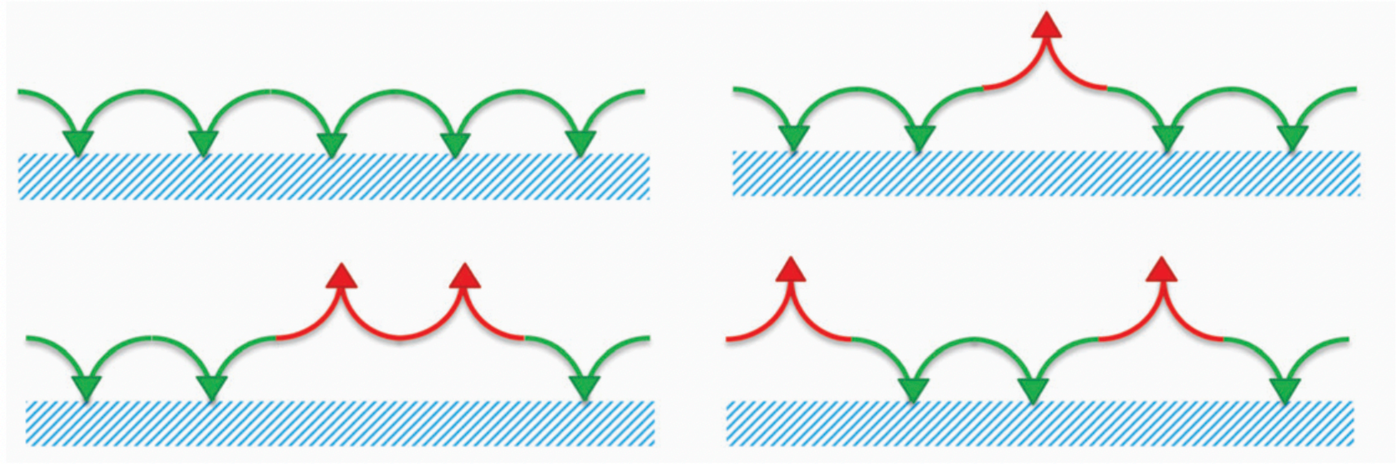

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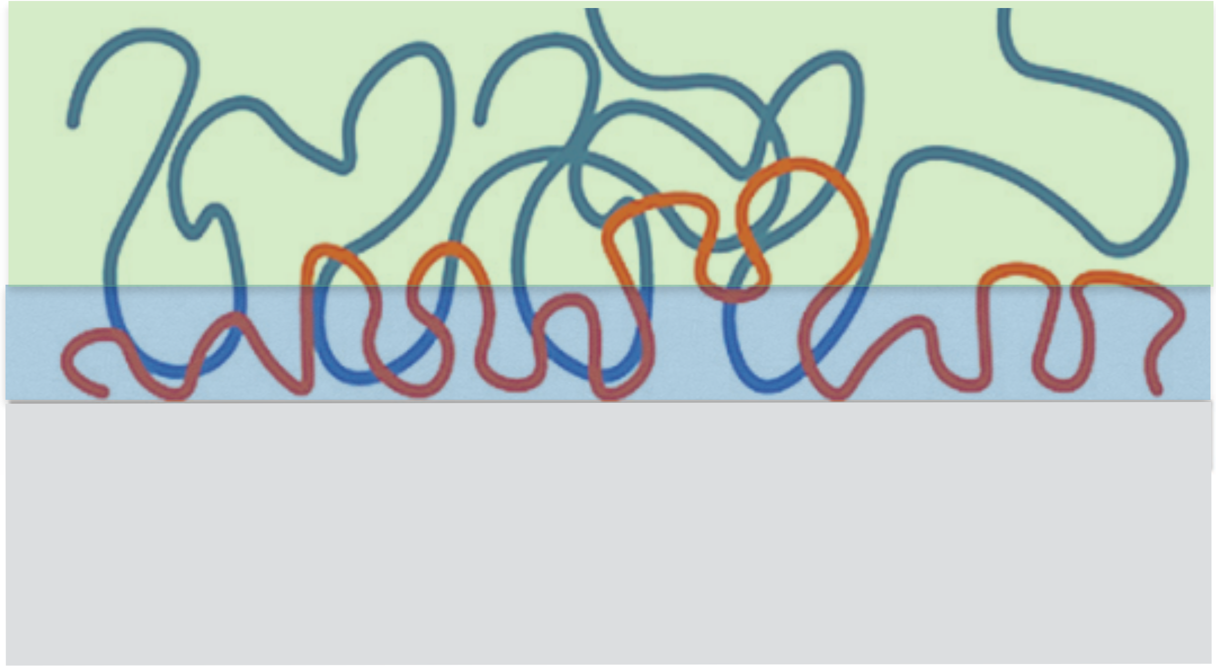


h_{ads}

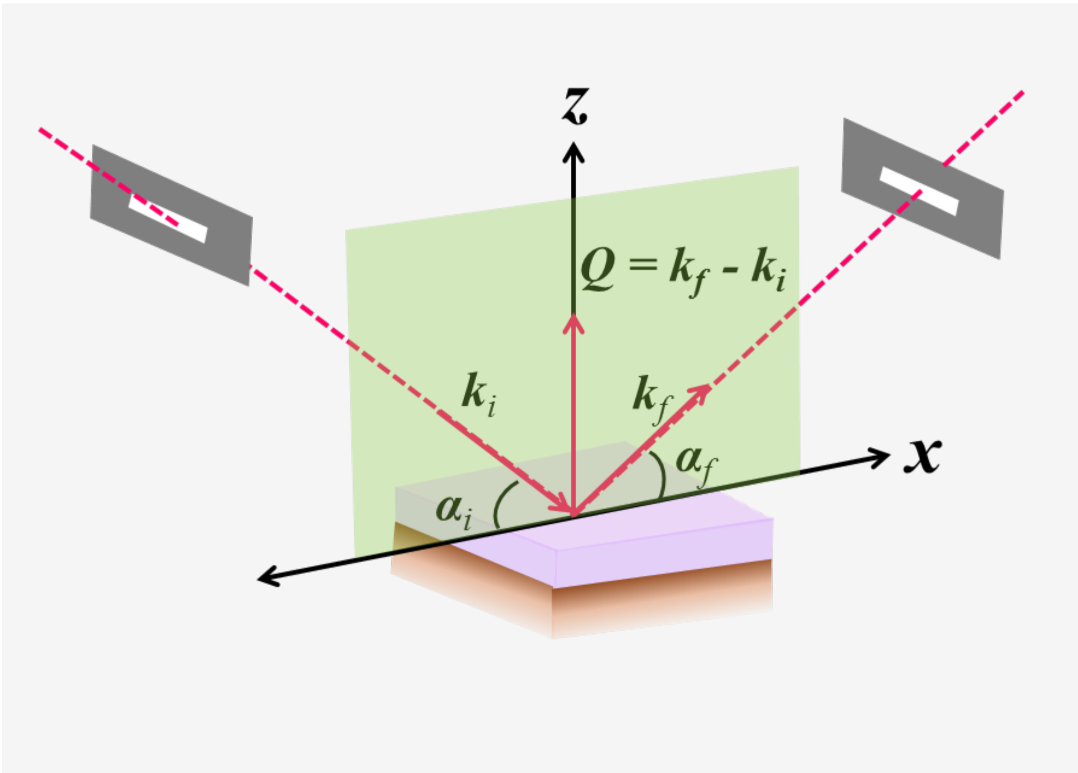
Adsorbed layer is buried and close to the impenetrable hard wall.

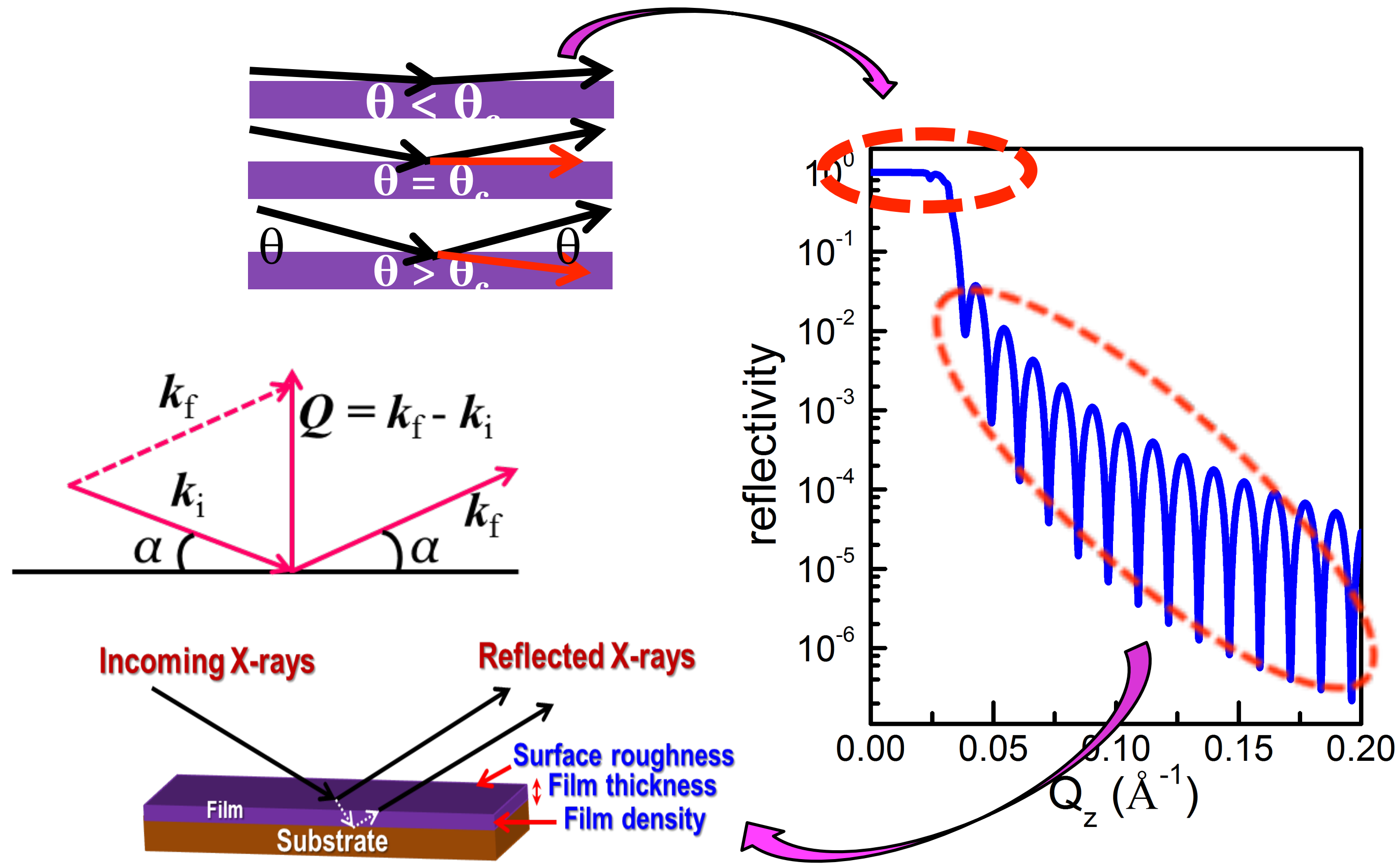
Experimentally challenging to gain detailed information.

Soft Matter, 2020, **16**, 5348–5365

Experimental techniques: XRR

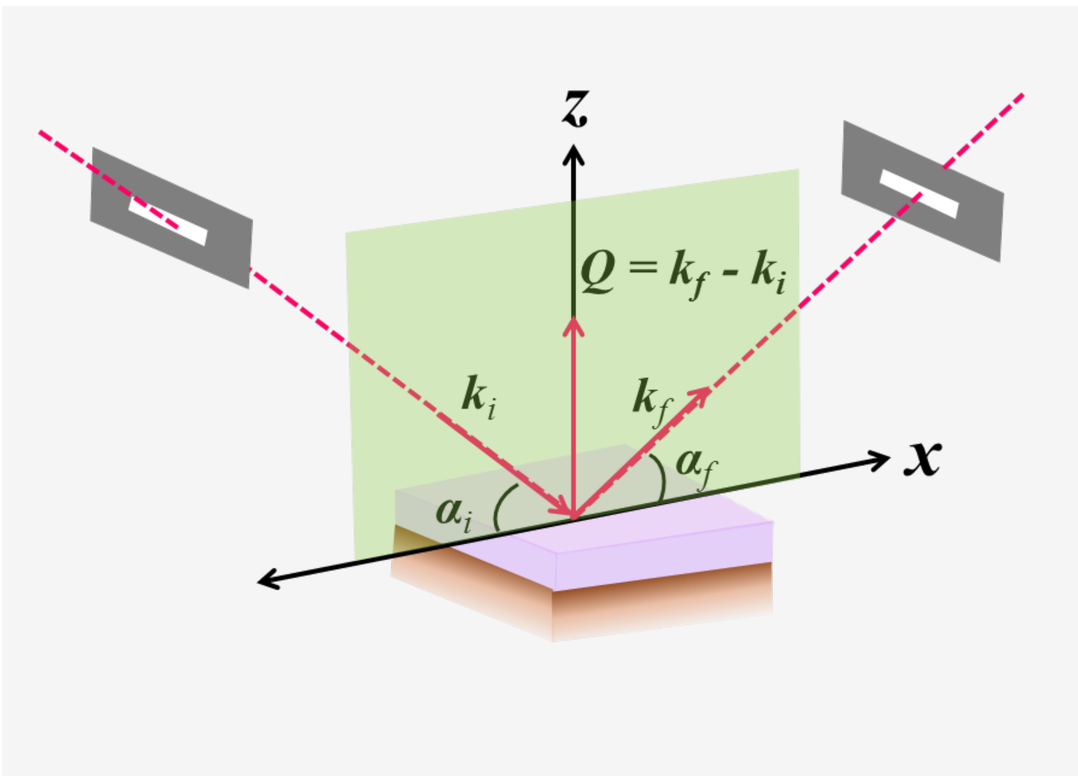
- **Specular X-ray Reflectivity (XRR)**

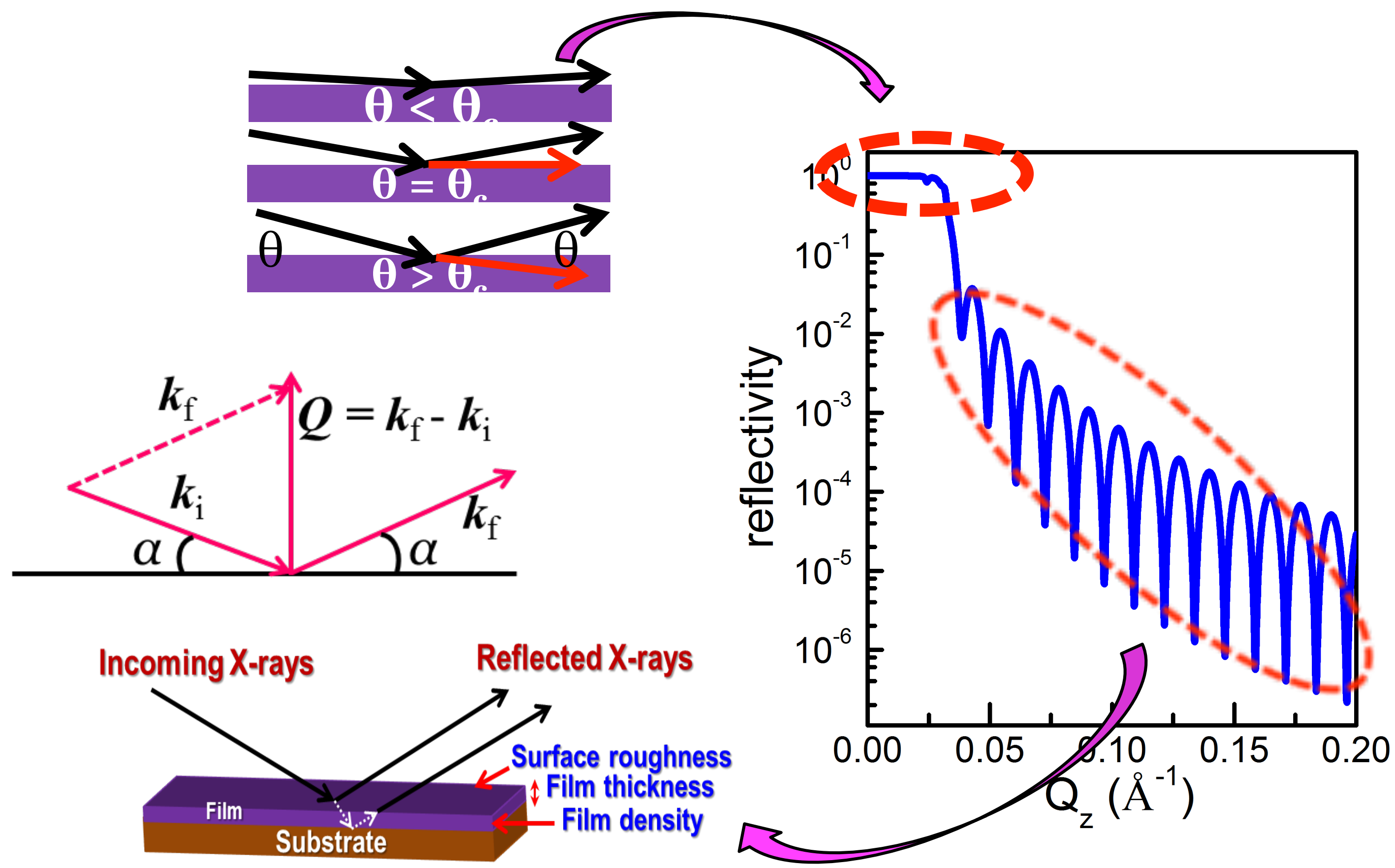




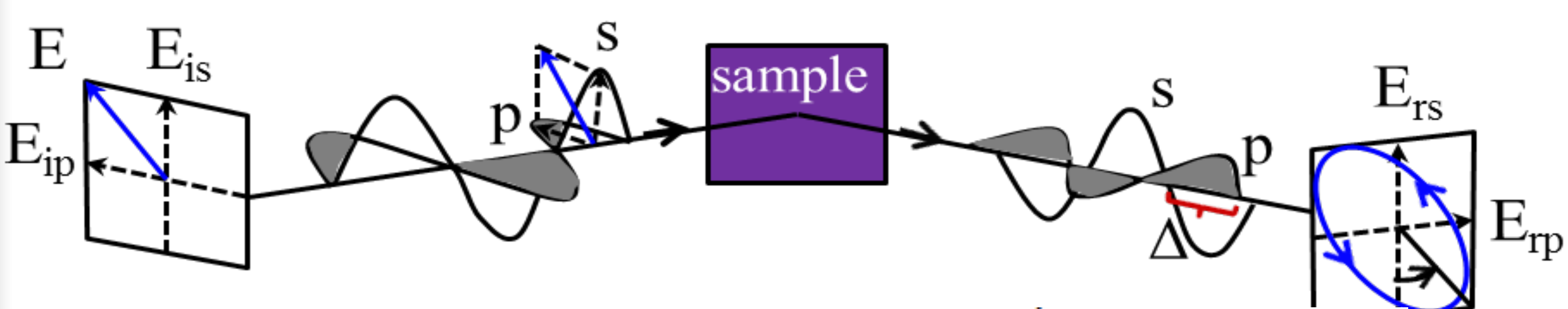
Experimental techniques: XRR & Ellipsometry

- **Specular X-ray Reflectivity (XRR)**

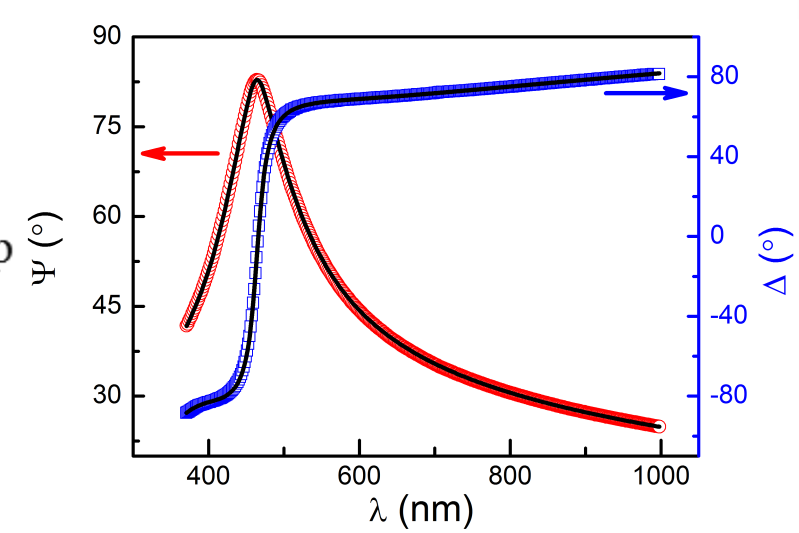




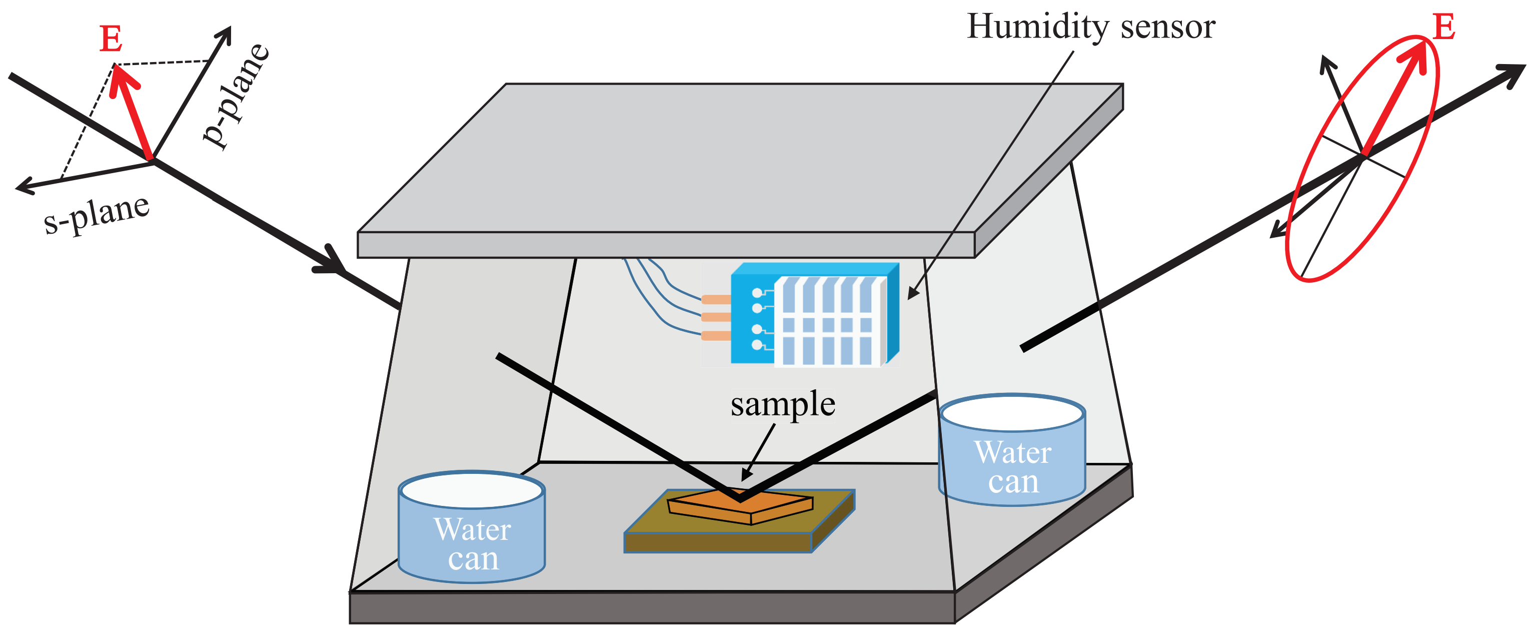
- **Spectroscopic Ellipsometry (SE)**

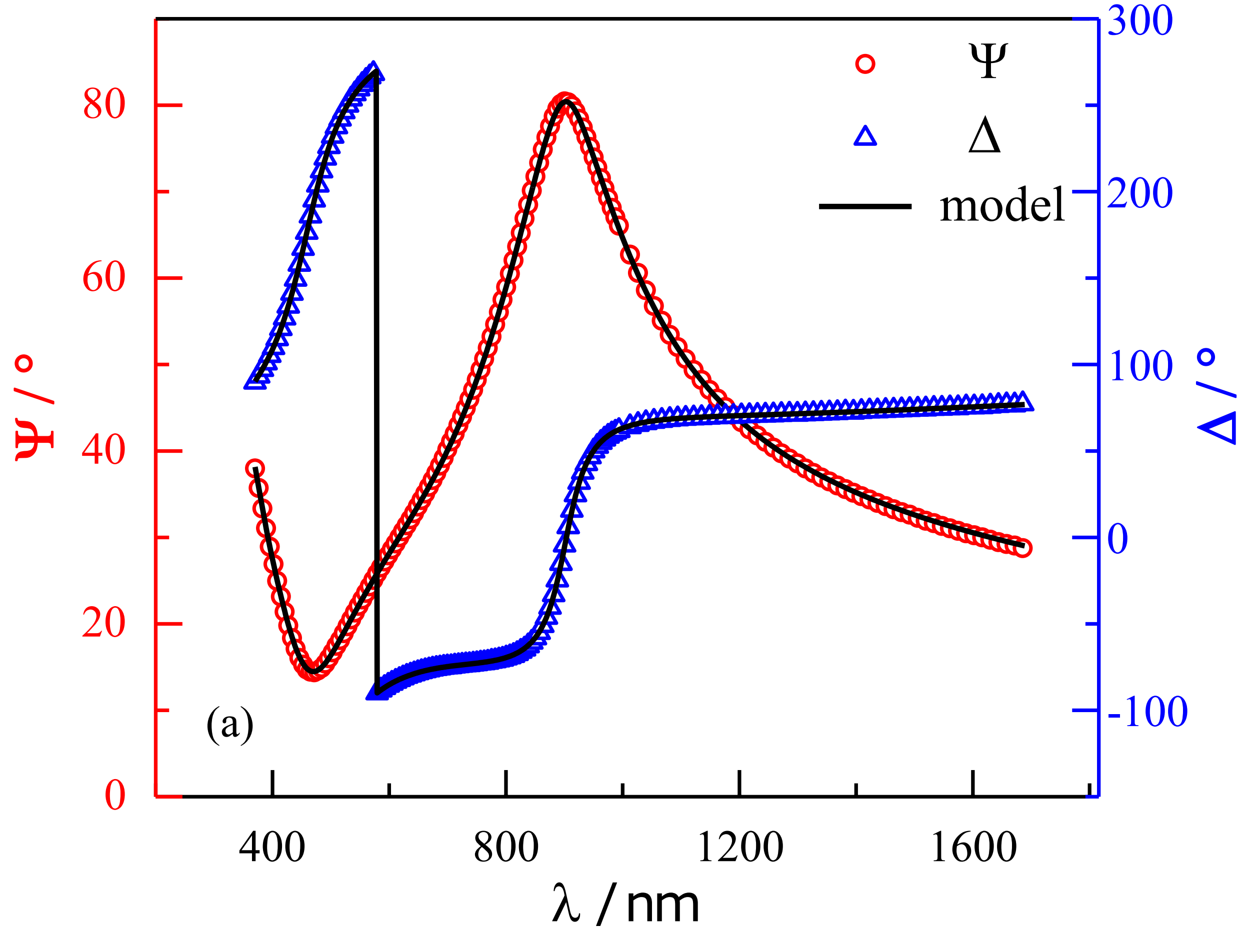


$$\rho \equiv \tan\Psi \exp(i\Delta) \equiv \frac{r_p}{r_s} \equiv \left(\frac{E_{rp}}{E_{ip}}\right) \Big/ \left(\frac{E_{rs}}{E_{is}}\right) = \frac{E_{rp}}{E_{rs}}$$

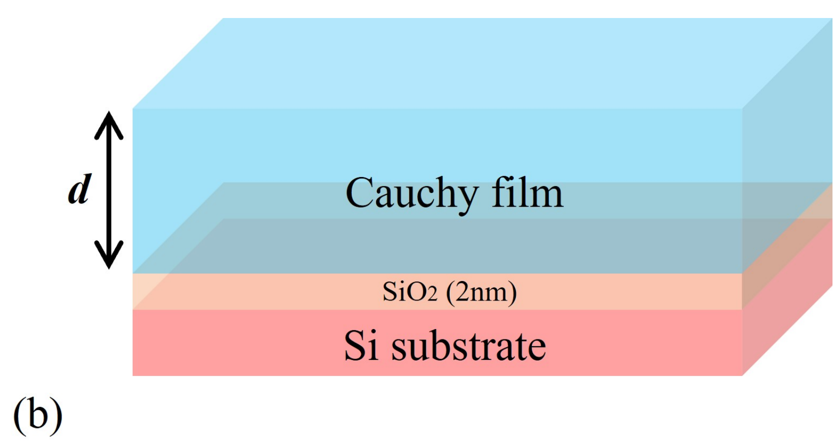


Measurement of thickness and refractive index

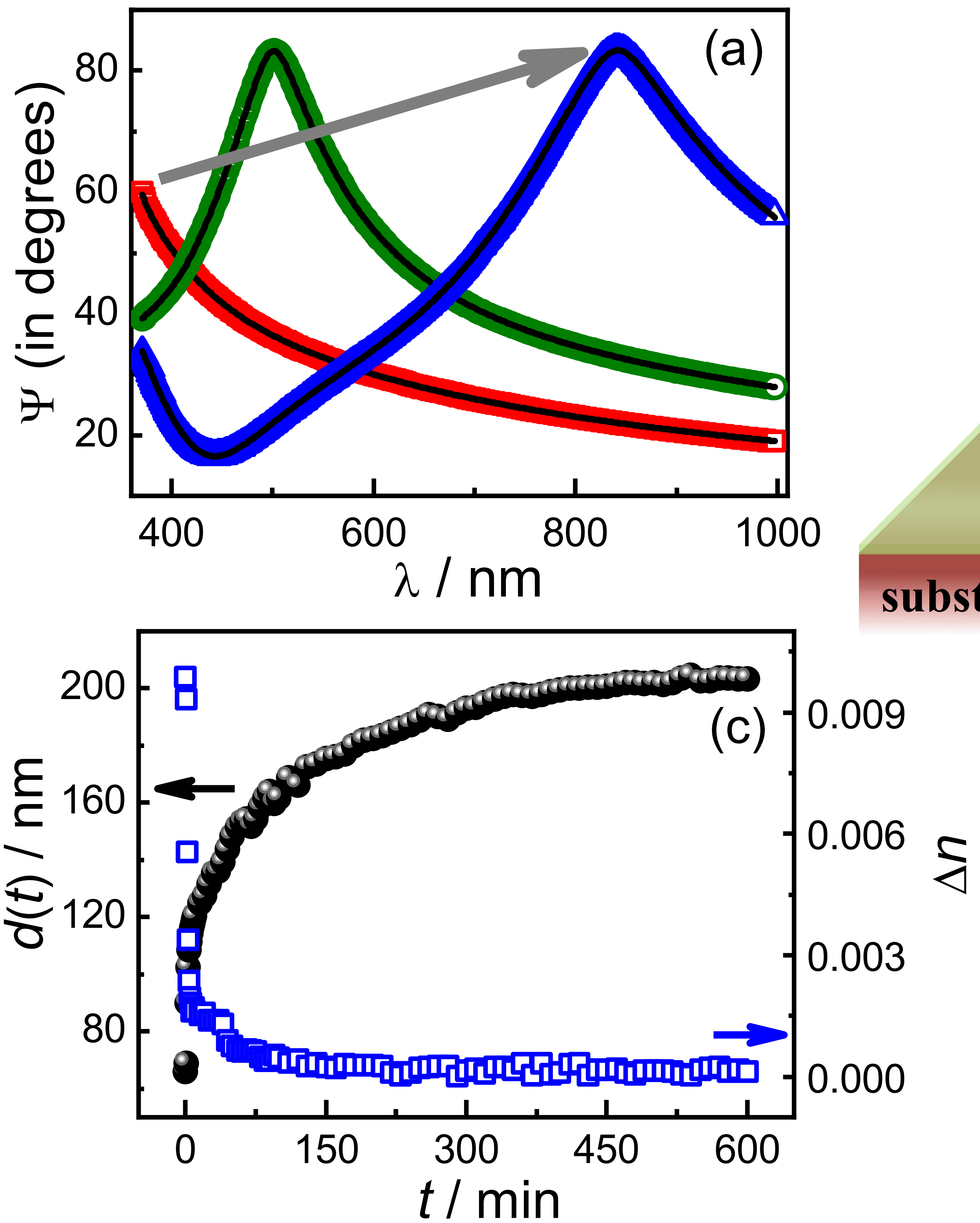


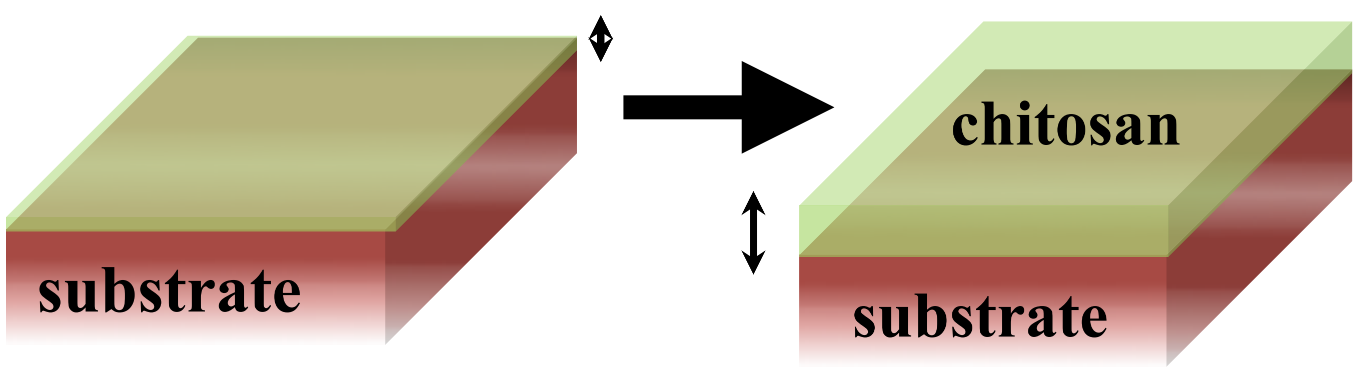


$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$$

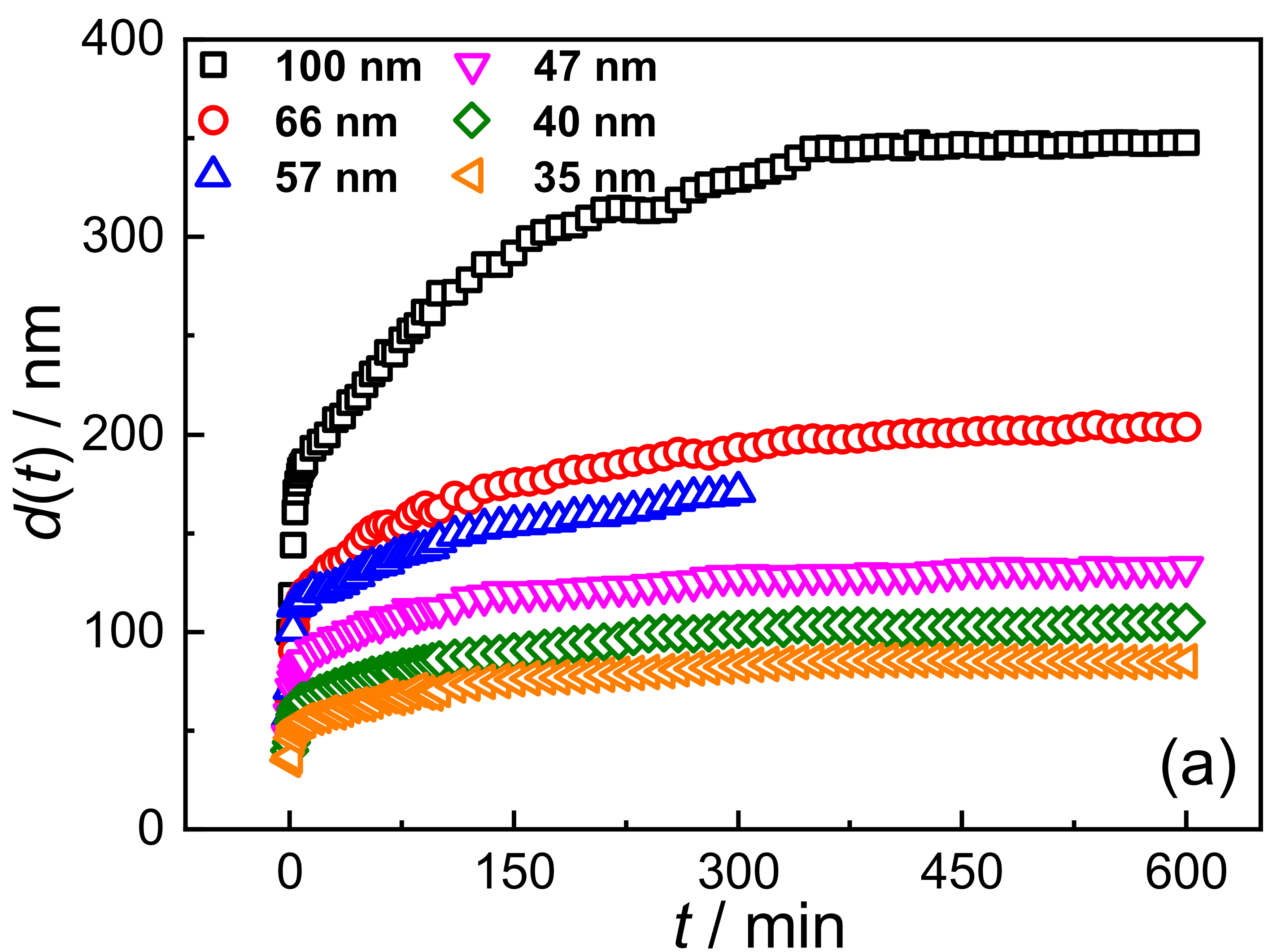


Quantification of Swelling





Time evolution of film thickness

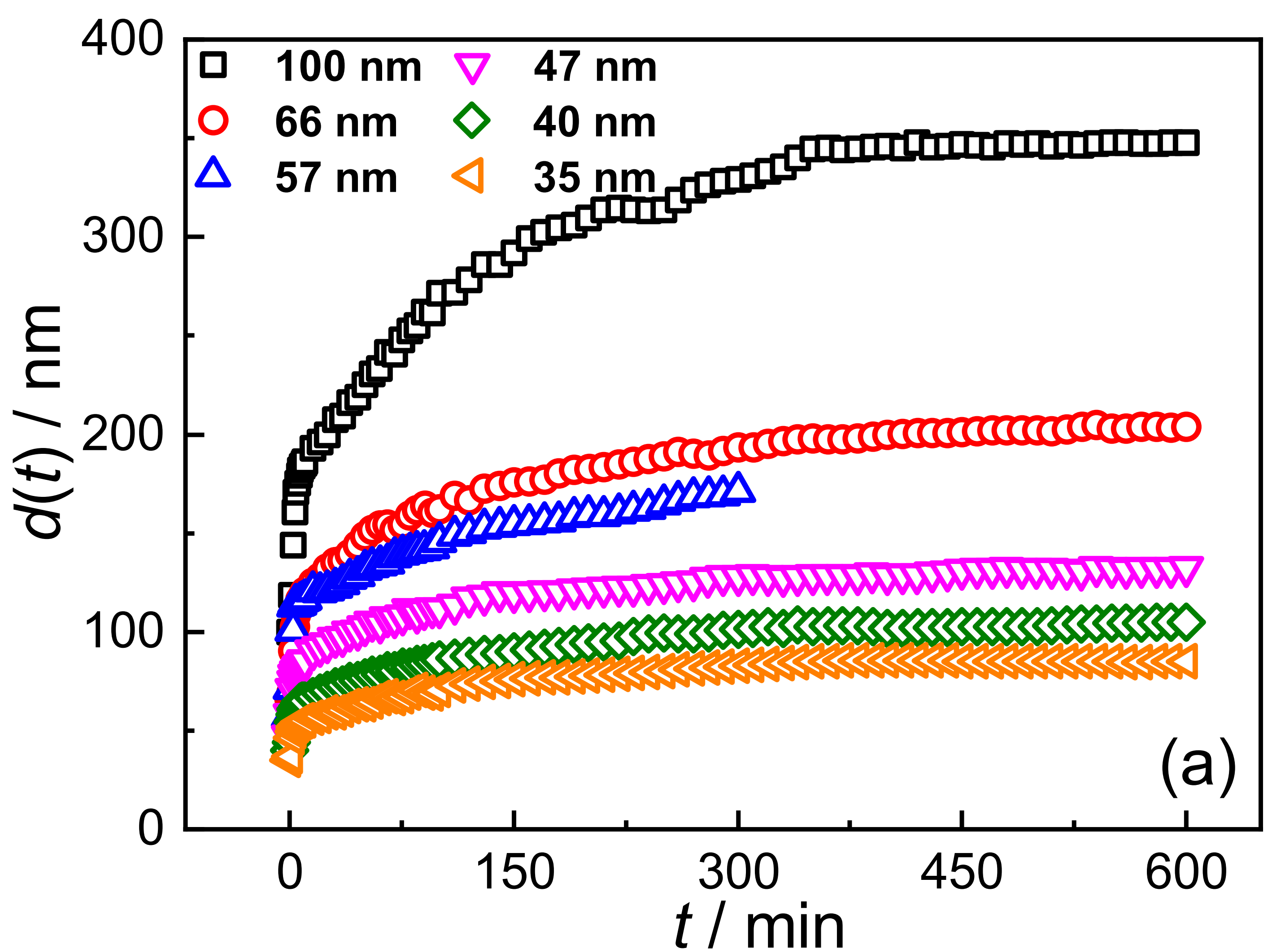


The asymptotic swelling ratio,

$$d(t \rightarrow \infty)/d(0)$$

increases with increasing initial film thickness *d(0)*

Time evolution of film thickness



The asymptotic swelling ratio,

$$d(t \rightarrow \infty)/d(0)$$

increases with increasing initial film thickness *d(0)*

This is surprising, because it should only depend on the experimental conditions, if swelling process can be described by thermodynamics parameters

Assumptions

1. Polymer chains adsorb onto the non-repelling Si/Si–O surface to form a compact layer that is strongly bound to the substrate

2. The thickness of the compact layer is independent of the initial thickness of the polymer film

3. The compact, strongly bound layer does not swell when exposed to solvent vapor

Effective swelling ratio

We define time-dependent "effective swelling ratio", c(t)

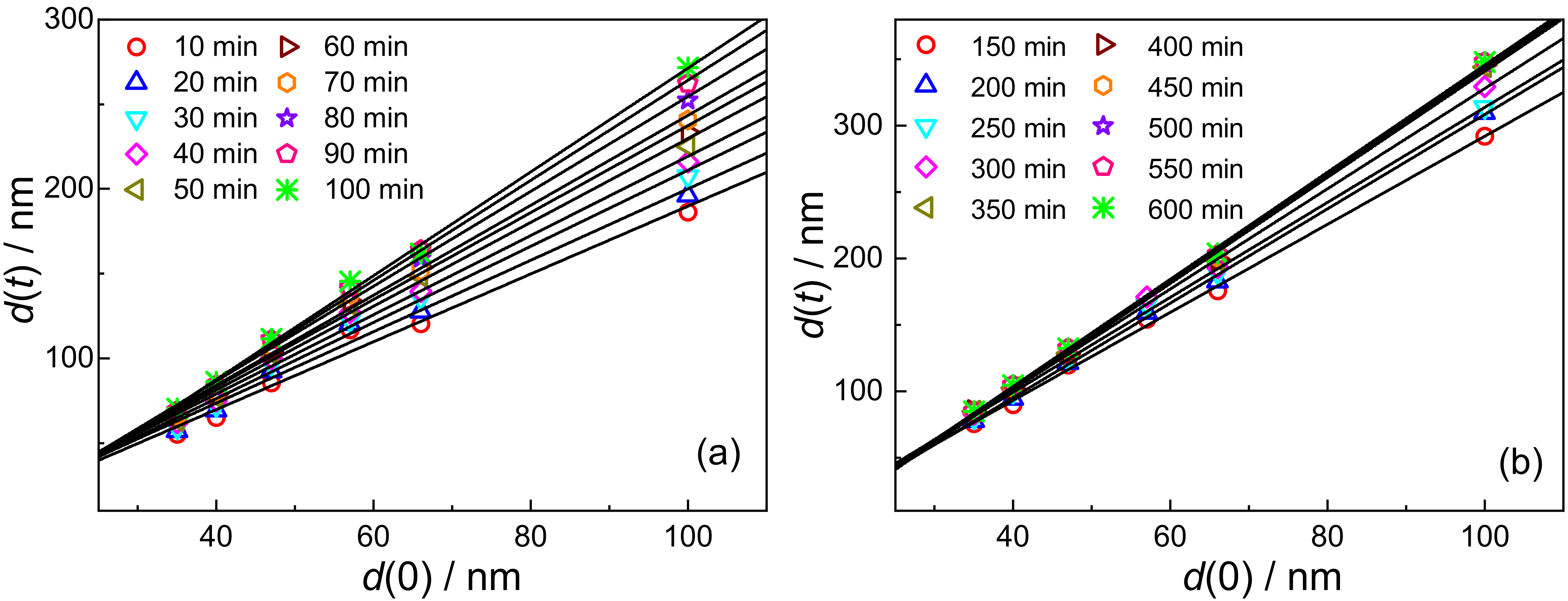
$$c(t) = \frac{d(t) - d_s}{d(0) - d_s}$$

and

$$d(t) = c(t)d(0) + (1 - c(t))d_s$$

This suggests that a plot of ***d(t)*** as a function of ***d(0)*** should be a **straight line with non-zero intercept**

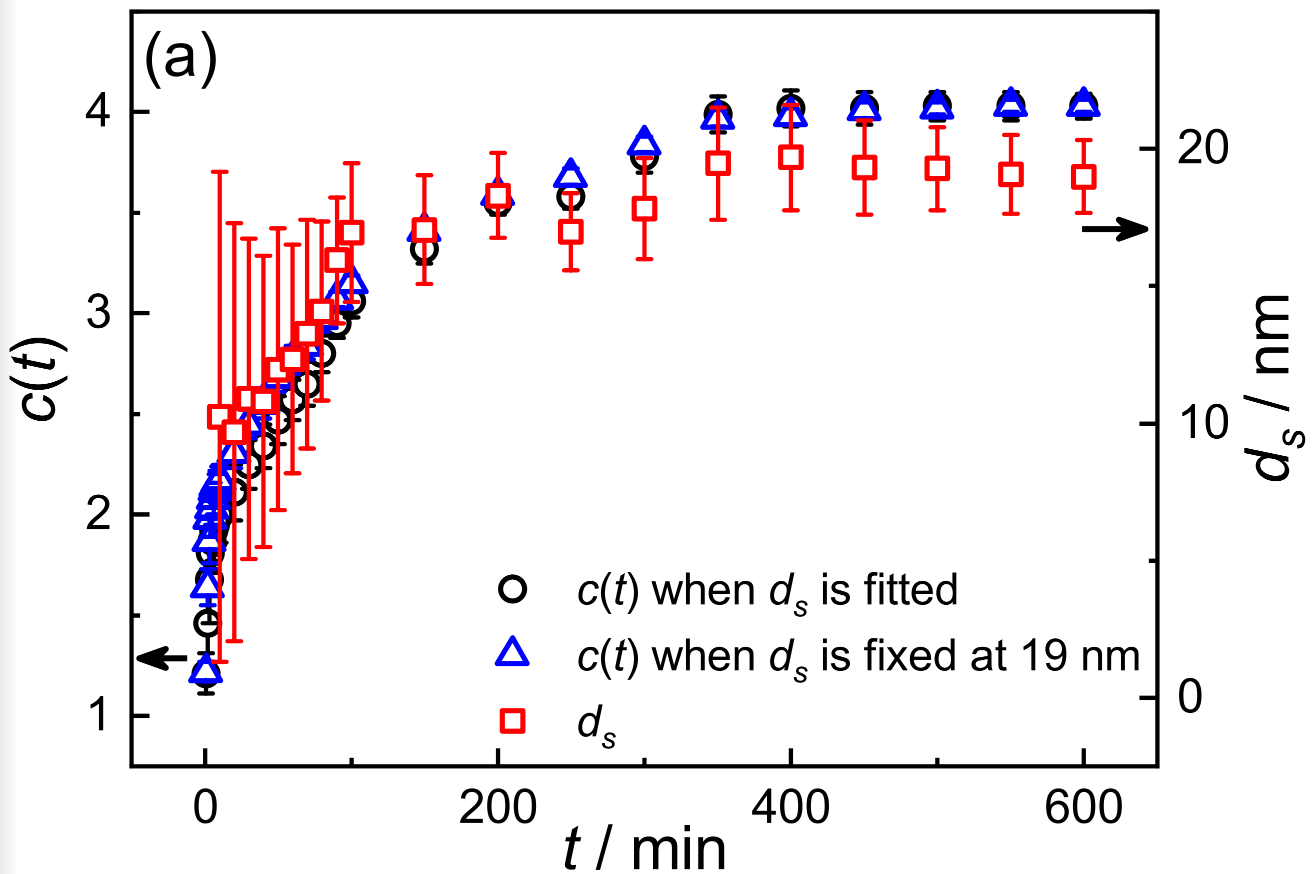
Dependence of swelling on d(0)



Indeed, it could effectively described by a straight line with non-zero intercept

P. Lairenjam, Sathish K. Sukumaran and D. K. Satapathy, Macromolecules, 54, 10931 (2021)

Effective swelling ratio and bound layer



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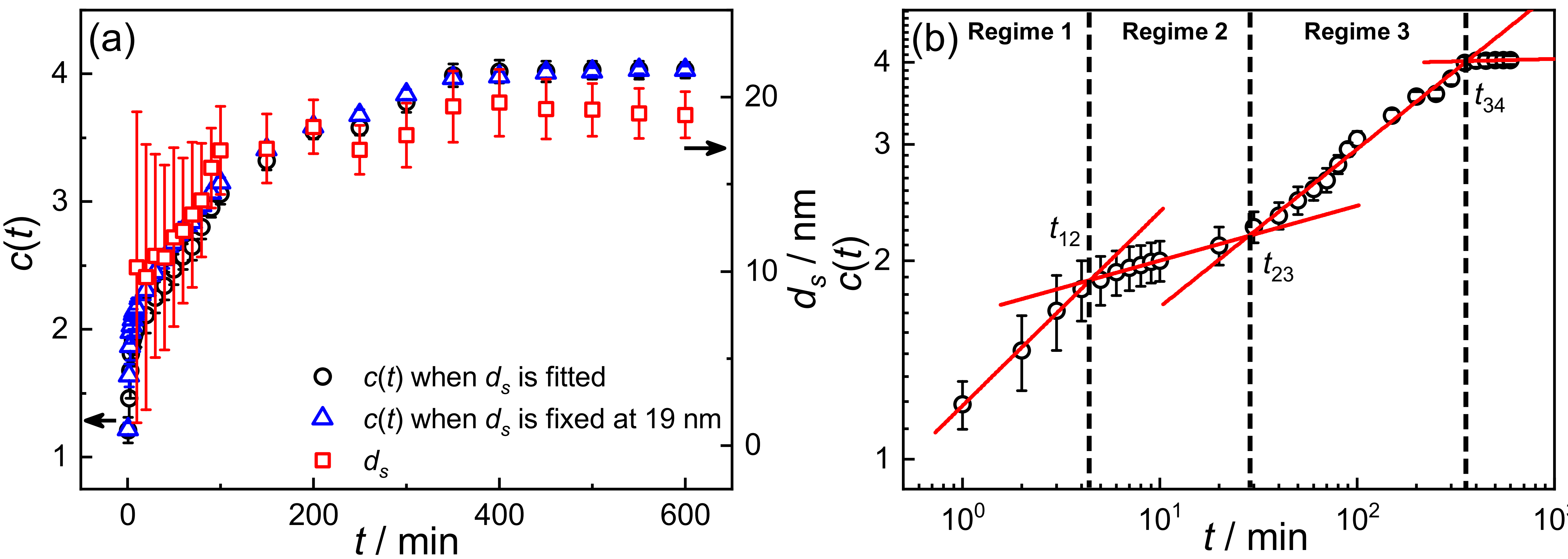
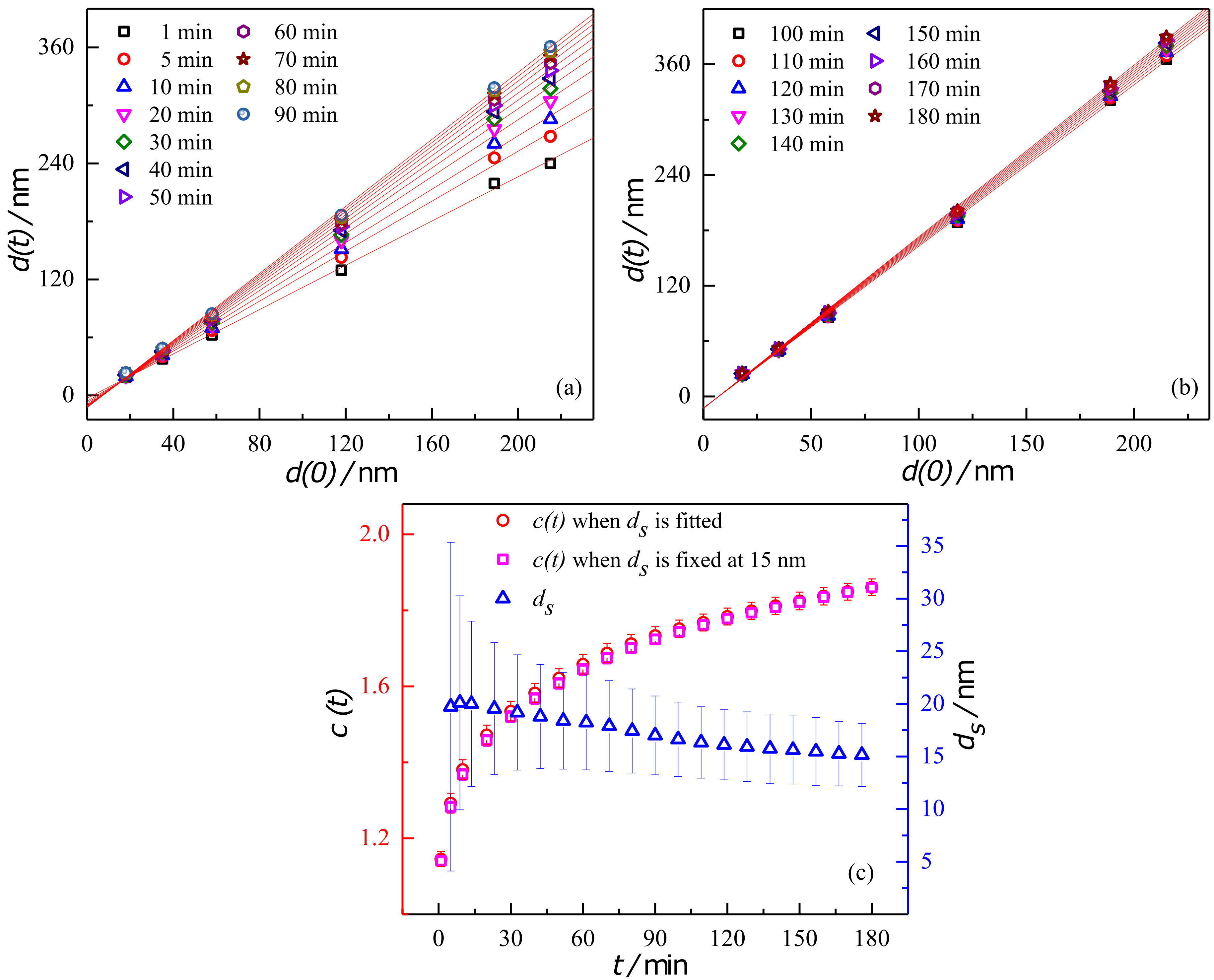


P. Lairenjam, Sathish K. Sukumaran and D. K. Satapathy, Macromolecules, 54, 10931 (2021)

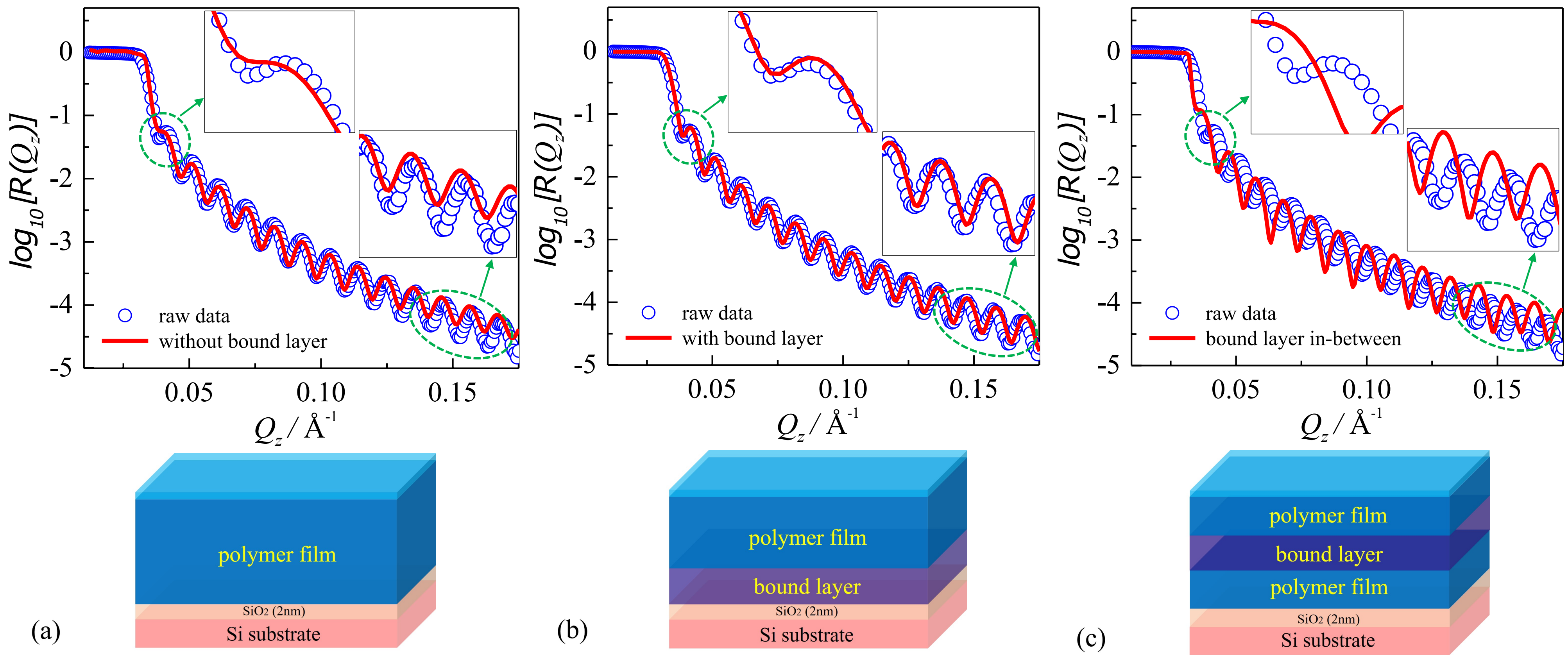
Collaboration with Prof Sathish K. Sukumaran, Yamagata Uni. Japan

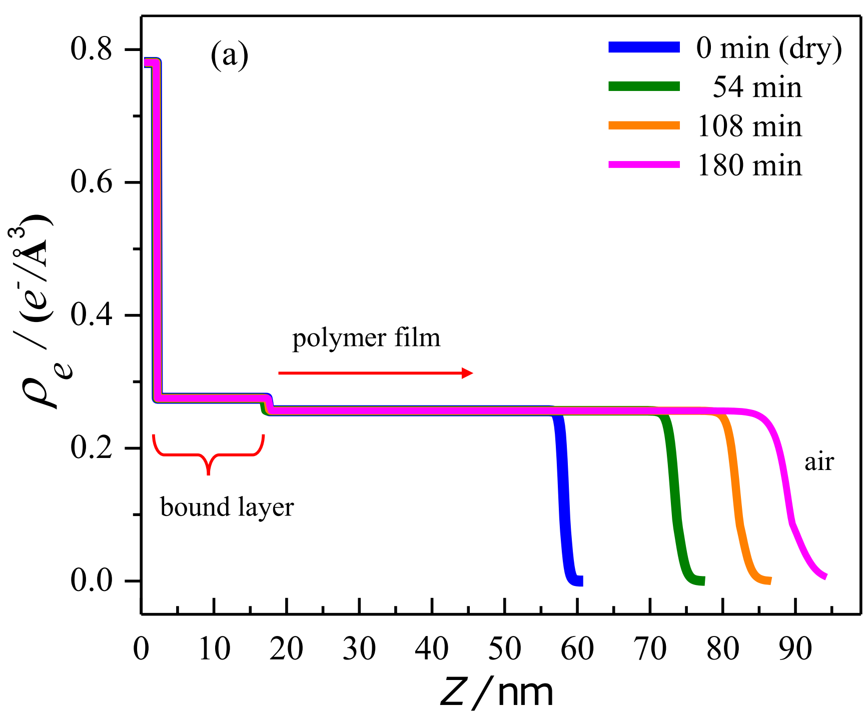
Effective swelling ratio: second polymer system



S. Z. Bhutia, P. Lairenjam, S. K. Sukumaran and D. K. Satapathy, Soft Matter, **19,** 3859 (2023)

Spatial location of compact bound layer : XRR





Small decrease in the electron density at Z ≈ 16 nm

consistent with the existence of a compact bound layer

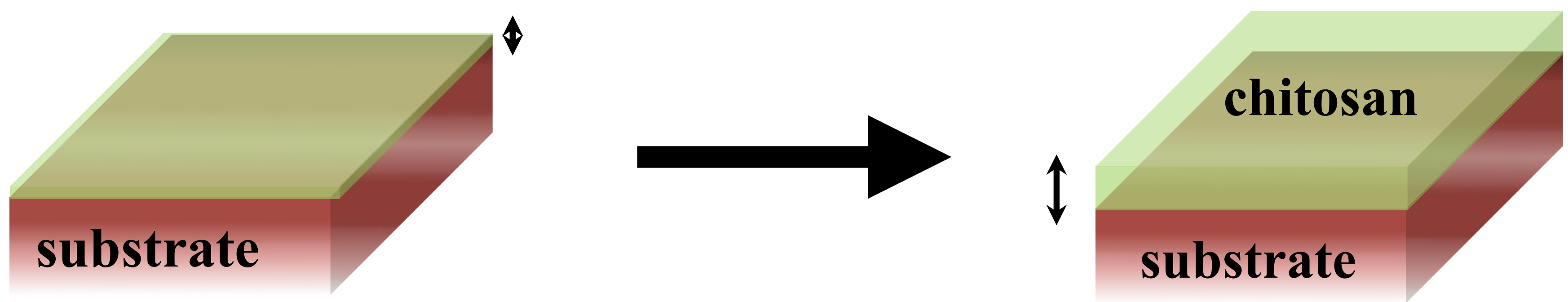
S. Z. Bhutia, P. Lairenjam, S. K. Sukumaran and D. K. Satapathy, Soft Matter, ***19,*** *3859 (2023)*

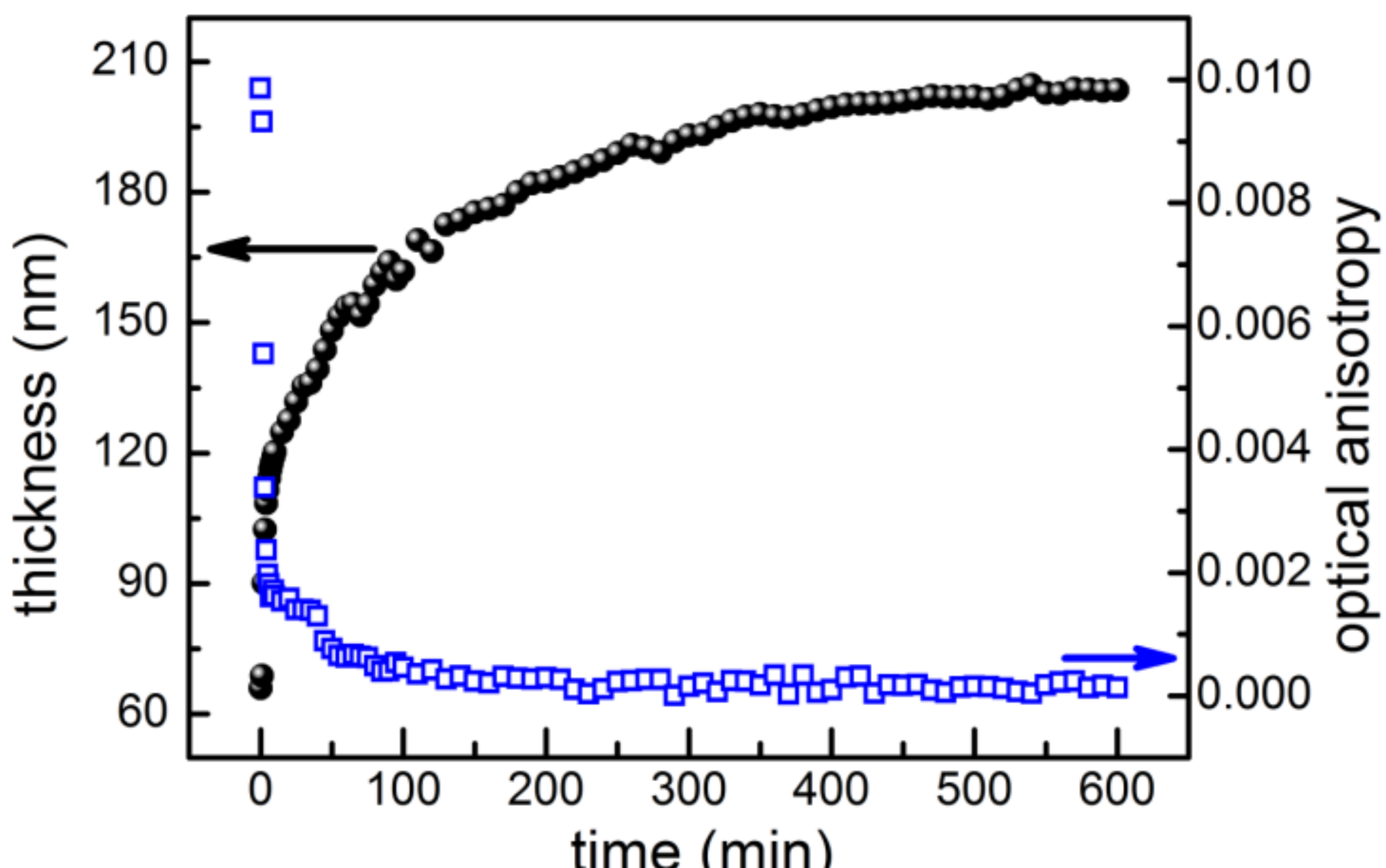
Conclusions

By assuming the existence of a **compact layer tightly bound (irreversibly adsorbed)** to the substrate surface and the swelling of the remaining portion of the chitosan film, the swelling of films of different $d(0)$ values could be described using a single function, $c(t)$.

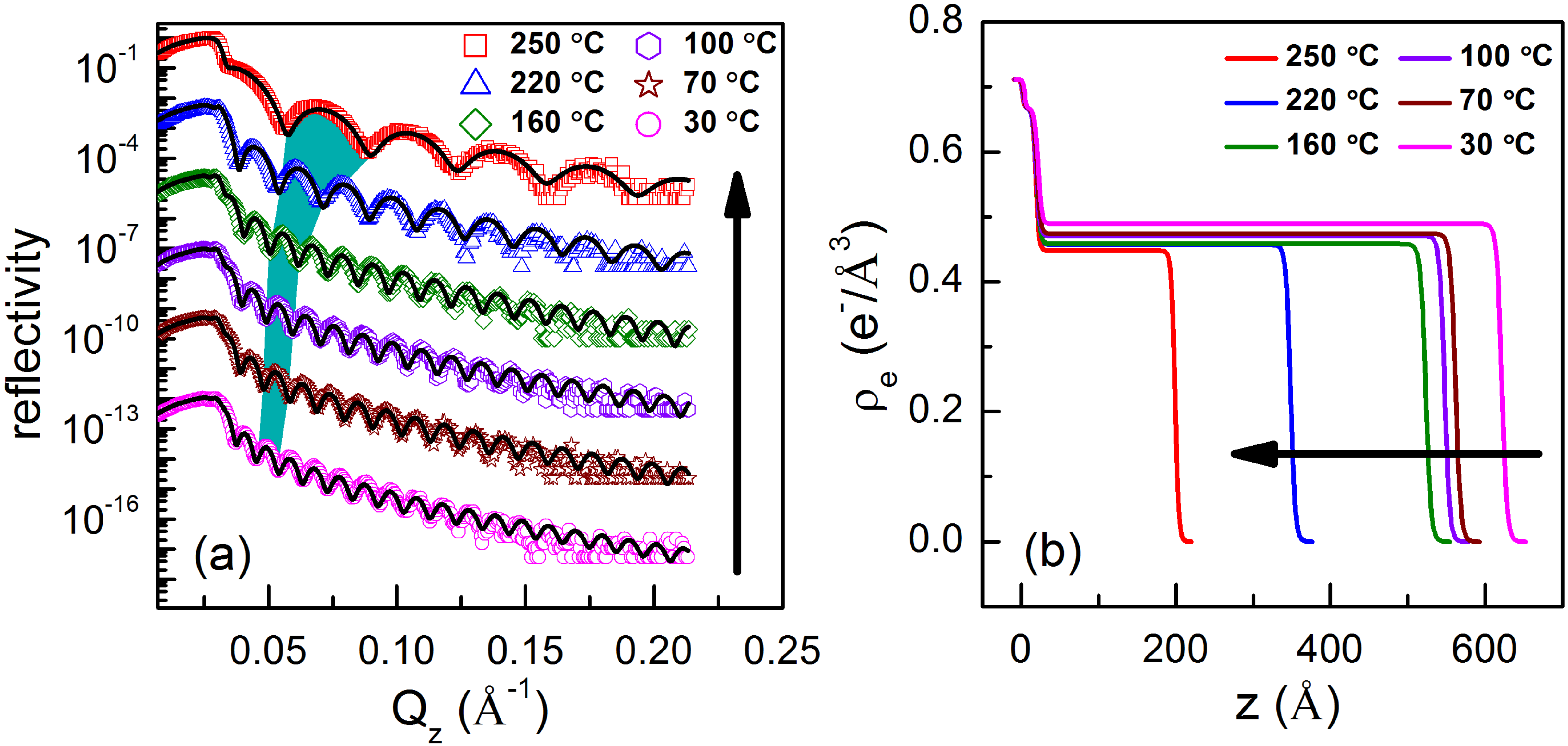
Water Desorption form confined Hydrogel Films

Swelling of the hydrogel film



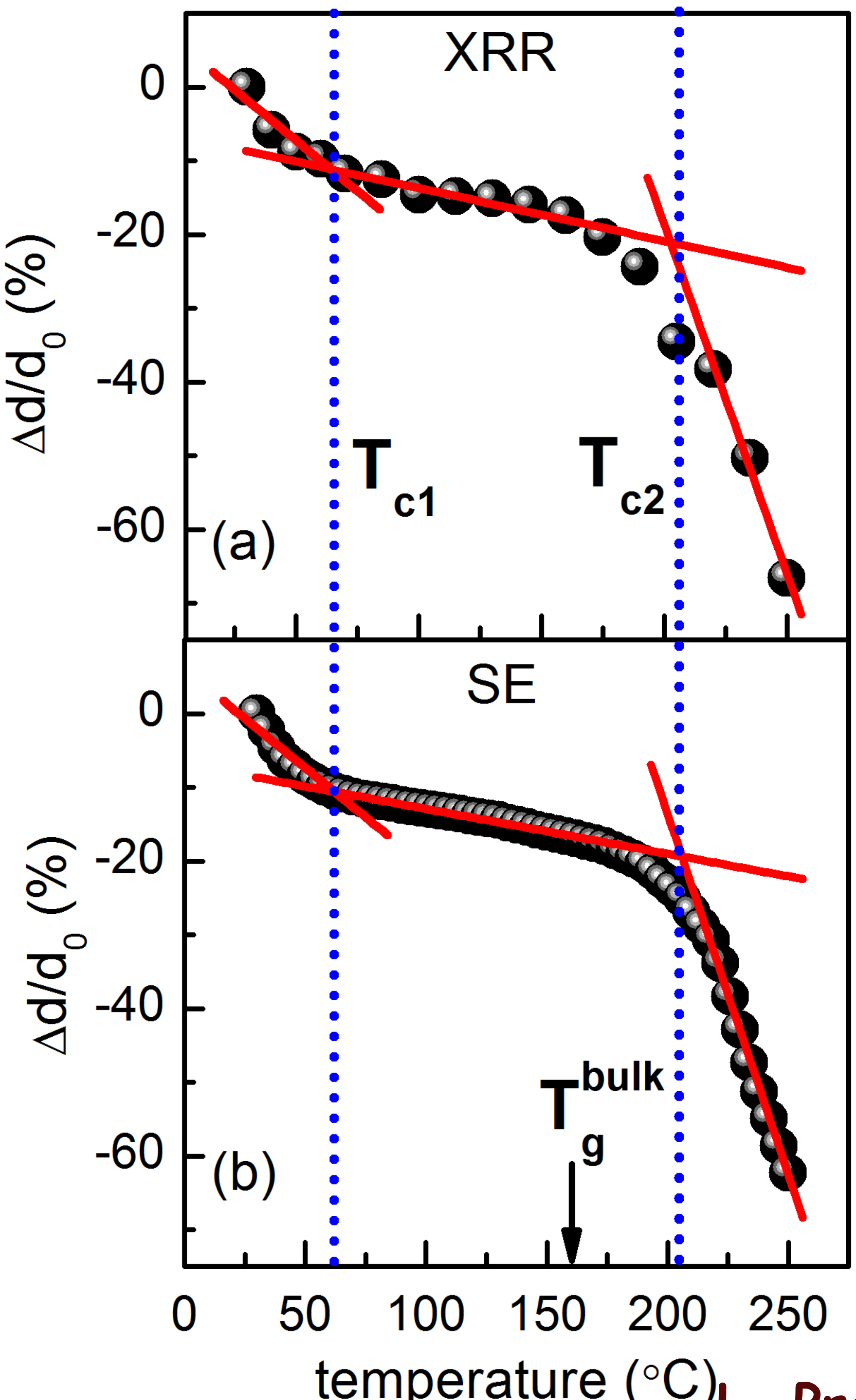


Water desorption : X-ray reflectivity



- Electron density at 30C is close to that of chitosan plus one water molecule per glucosamine unit
- Electron density at 210C, matches with almost dry chitosan

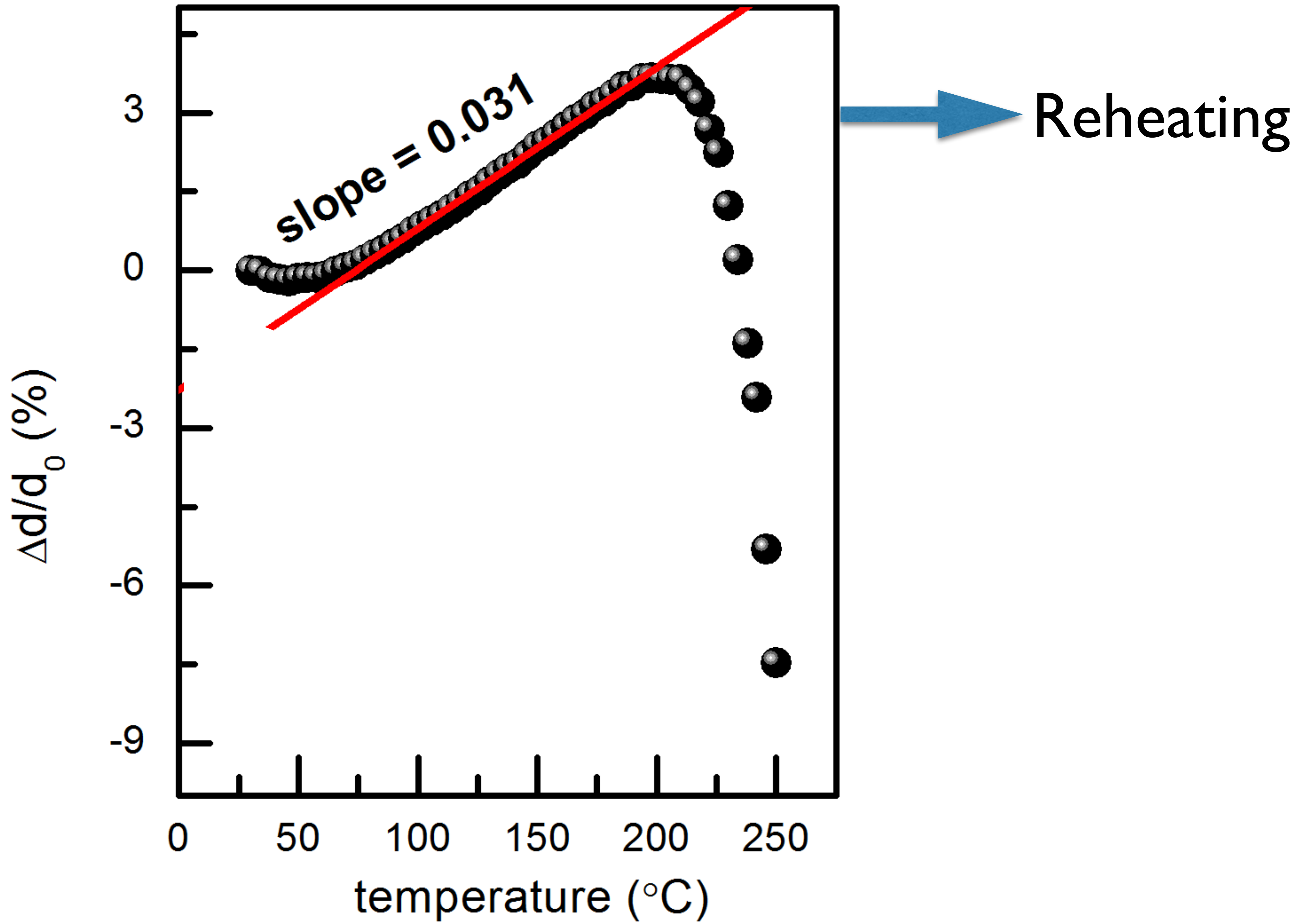
Water desorption : Characteristic Temperatures



- Large ~ 65% decrease in thickness
- Three different slopes
- Slow desorption of water followed by the even slower desorption and finally fast desorption

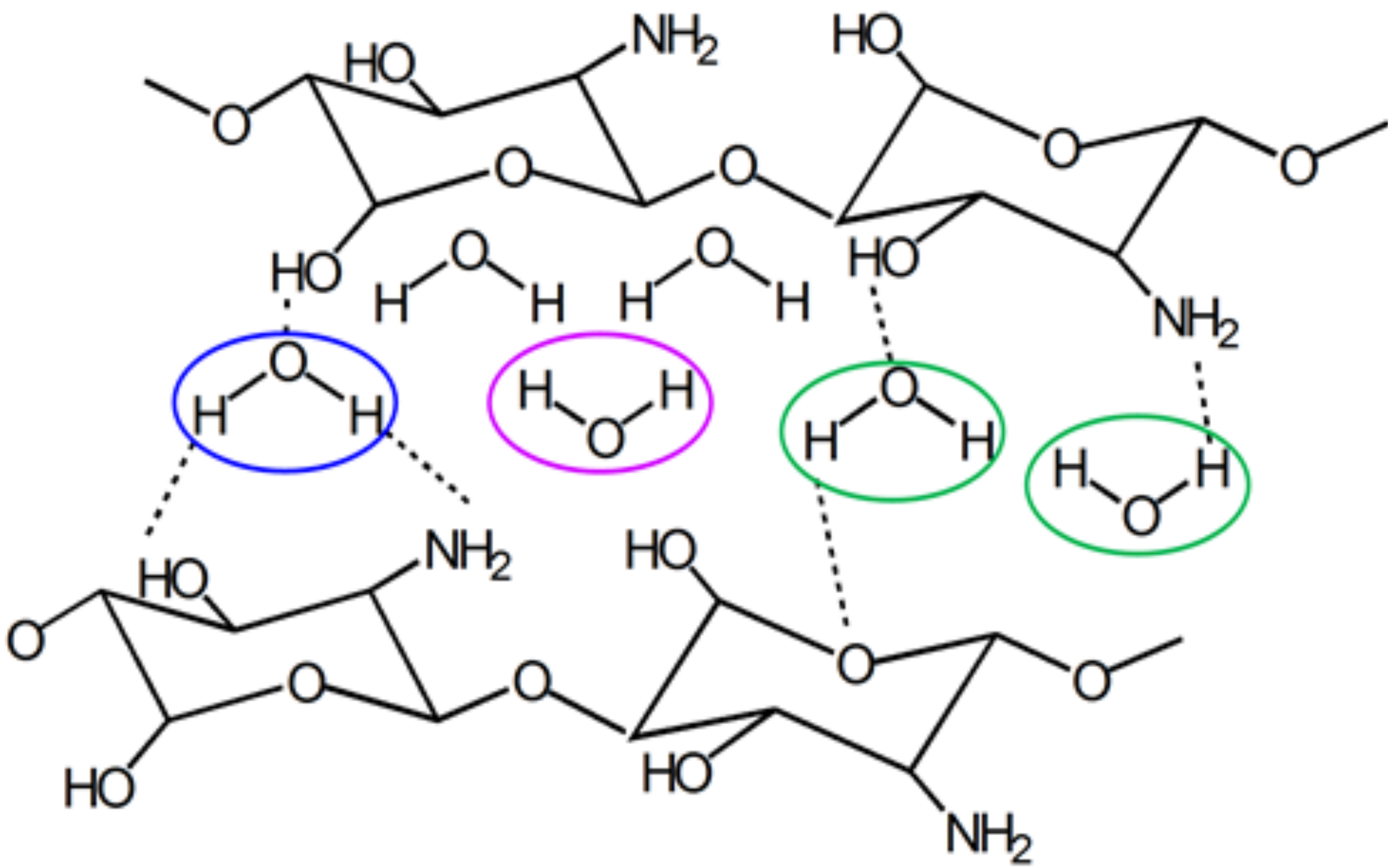
L. Pradipkanti et al. Soft Matter, 14, 2163 (2018)

Re-heating confirms complete water removal



L. Pradipkanti et al. Soft Matter, 14, 2163 (2018)

Different kinds of water in polymer matrix



Water binds to Amino and hydroxyl groups

E. López-Chávez et al. Polymer,2005, 46, 7519–7527

Different types of water in polymer matrix

Chitosan-water interaction is measured/estimated

Dielectric spectroscopy,
DSC,
Sorption isotherms and MD simulations

Co-existence of three kinds of water:

(i) Free water

(ii) Freezable bound water

(iii) Non-freezable bound water

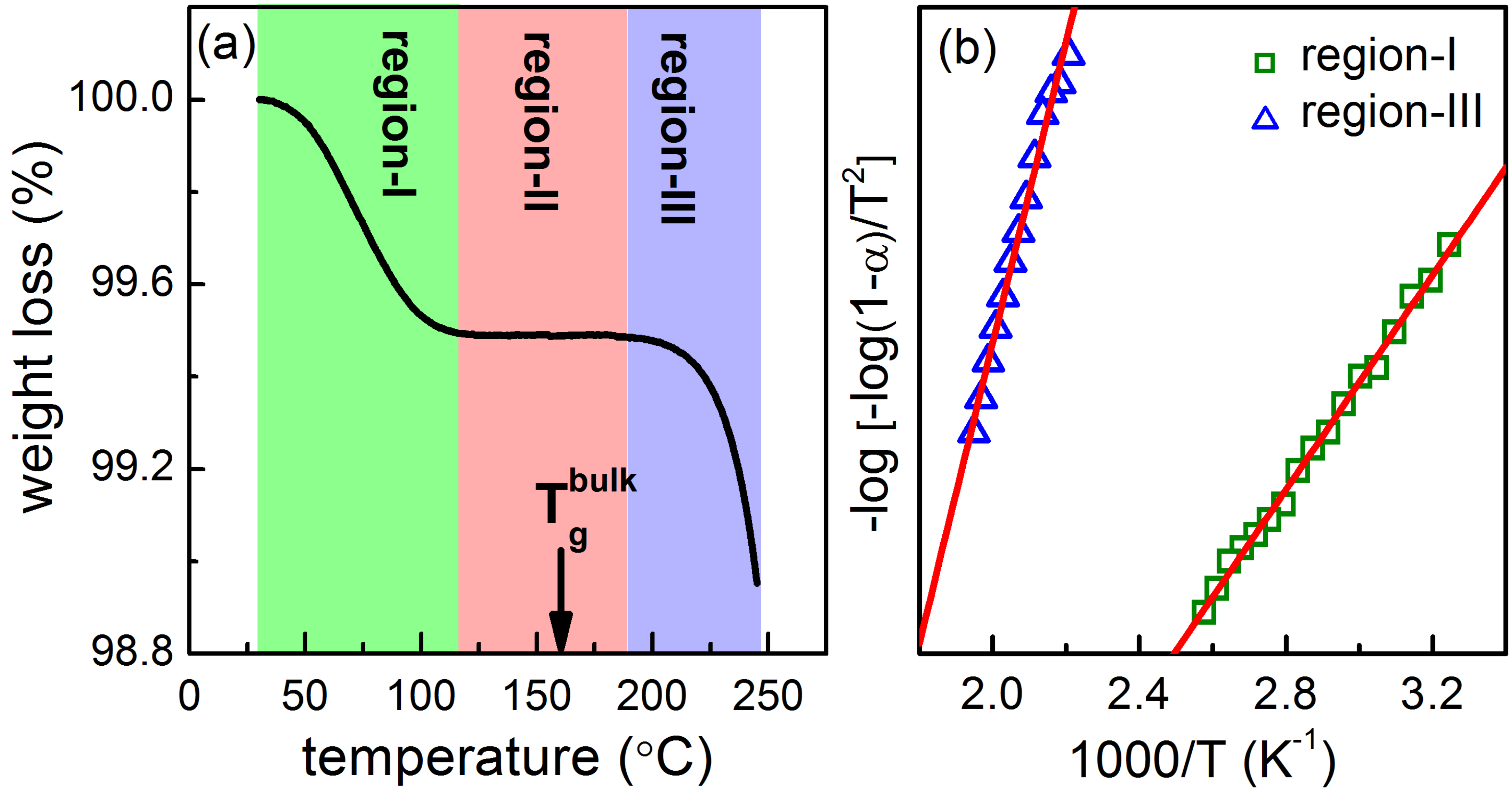
Non-freezable bound water forms first followed by freezable bound water and finally free water from

E. López-Chávez et al. Polymer, 2005, 46, 7519–7527,
H. Hatakeyama and T. Hatakeyama, Thermochim. Acta, 1998, 308, 3–22.

Different types of water in polymer matrix

Taking into account the enthalpy of hydration of
amino (70.3 kJ/ mol) and **hydroxyl (23.9 kJ/mol),** groups and
assuming that the enthalpy of hydration is equivalent
to that of dehydration,

the enthalpies of dehydration for type
water are estimated to be
94 kJ/mol and 165 kJ/mol, respectively.

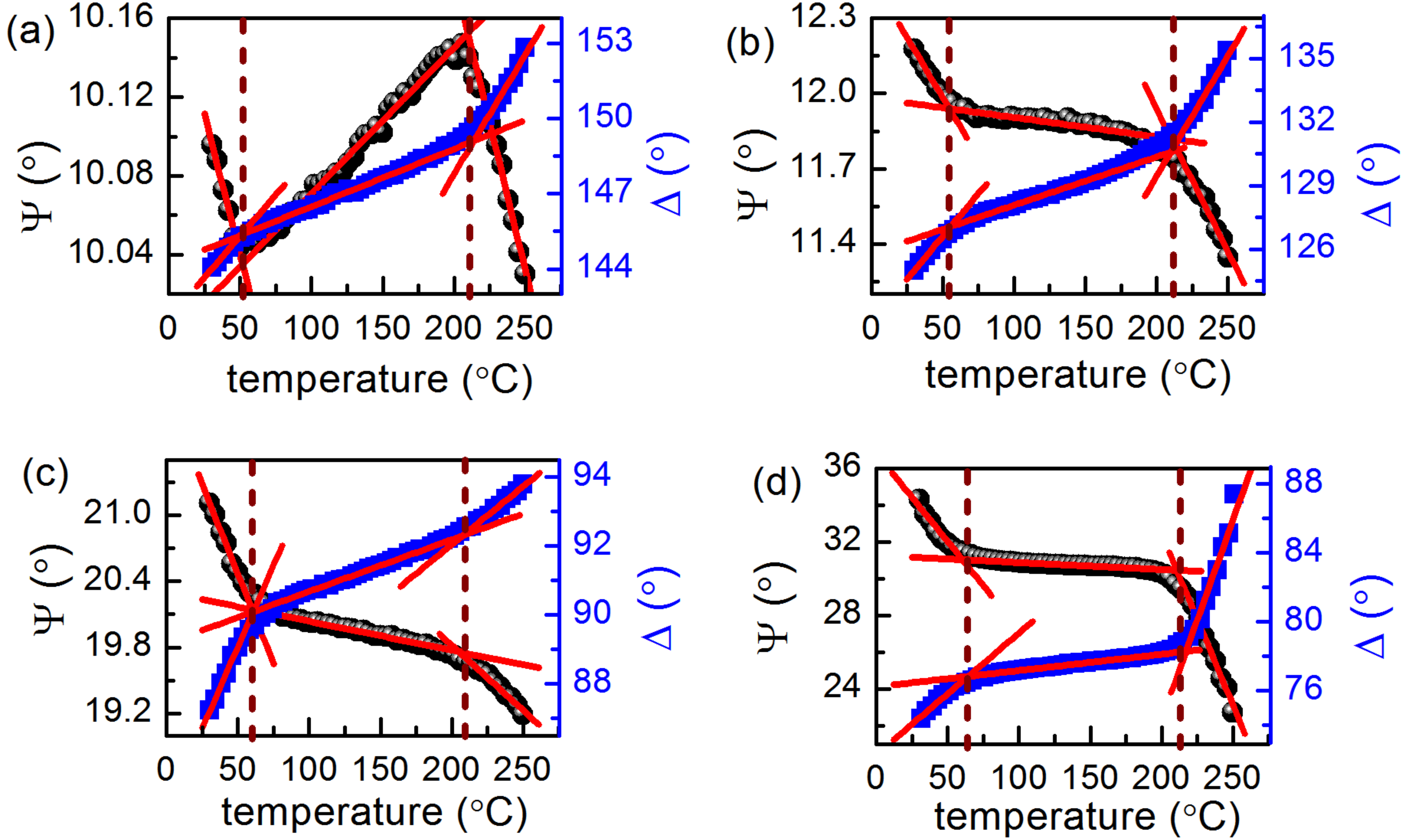


$$\alpha = \frac{W_0 - W_T}{W_0 - W_f},$$

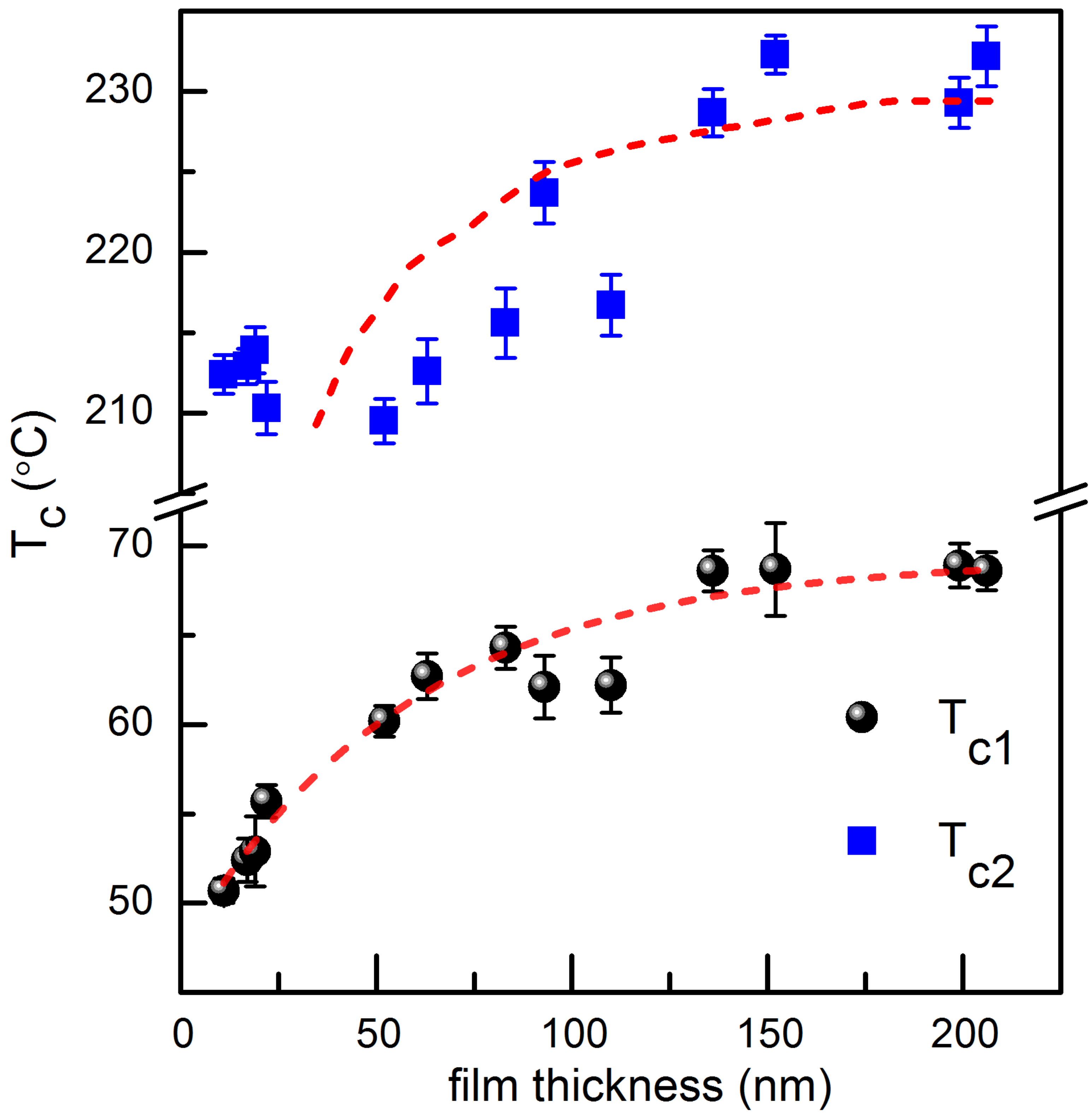
Activation energy (region I) = 60 kJ/mol

(region III) = 158 kJ/mol

A. W. Coats and J. Redfern, *Nature*, 1964, 201, 68–69.


(a)
10.16
10.12
10.08
10.04
Ψ (°)
153
150
147
144
Δ (°)
0 50 100 150 200 250
temperature (°C)
(b)
12.3
12.0
11.7
11.4
Ψ (°)
135
132
129
126
Δ (°)
0 50 100 150 200 250
temperature (°C)
(c)
21.0
20.4
19.8
19.2
Ψ (°)
94
92
90
88
Δ (°)
0 50 100 150 200 250
temperature (°C)
(d)
36
32
28
24
Ψ (°)
88
84
80
76
Δ (°)
0 50 100 150 200 250
temperature (°C)

Effect of confinement on water desorption



L. Pradipkanti et al. Soft Matter, 14, 2163 (2018)

Conclusions

- Water desorption phenomenon in chitosan thin films is investigated in detail by performing temperature dependent X-ray reflectivity and spectroscopic ellipsometry.

- Water desorption occurs at three distinct rates.

- Strong correlation exists between characteristic temperatures and the film thickness, i.e. the Tc decrease with decreasing film

Nissan-IITM research cell

IMPRINT- India Initiative

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