Partial Crystallinity in Alkyl Side Chain Polymers

A. Dhinojwala and coworkers

Phys. Rev. Lett. ***90****, 215501 (2003),*
Phys. Rev. Lett. ***101****, 065505 (2008)*

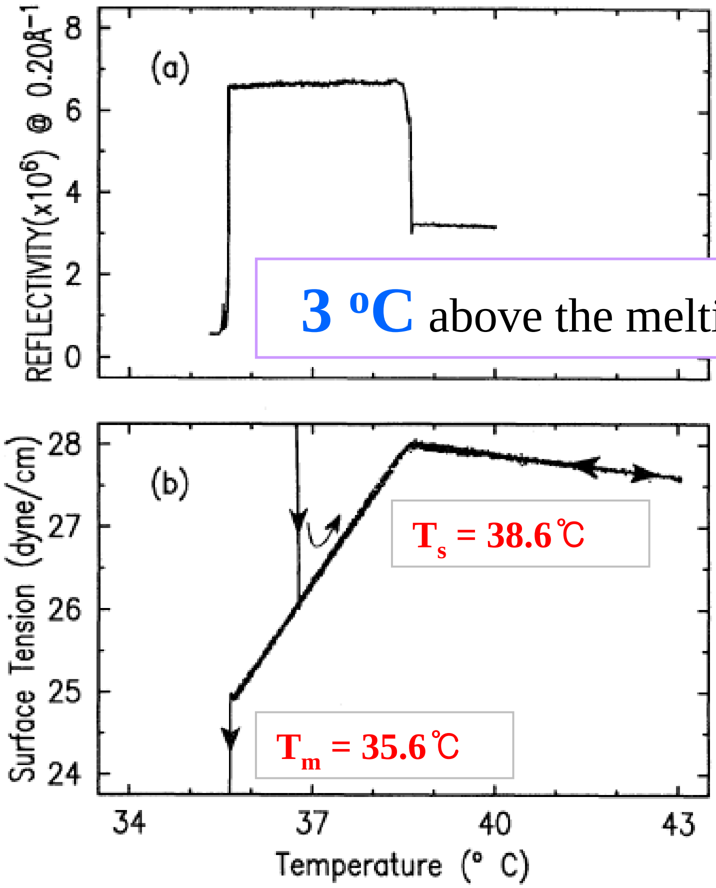
발표자 : 전윤남

11th Oct. 2008

Soft-Matter Optical Spectroscopy

Introduction : Surface freezing of alkanes

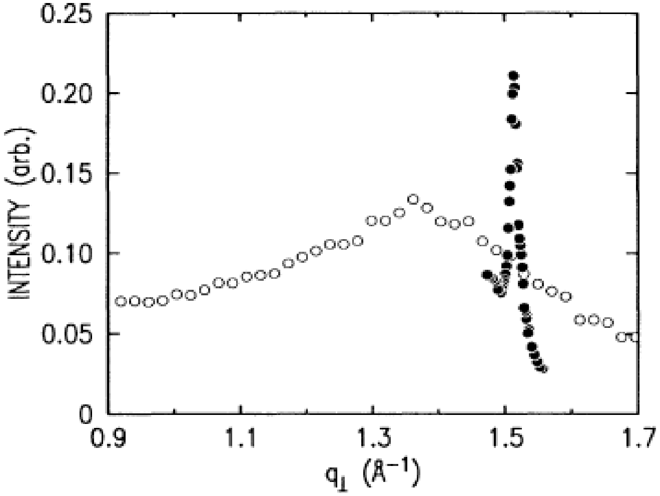
X. Z. Wu et al., Phys. Rev. Lett, **70**, 958 (1993)



3 °C above the melting temp.

T_s = 38.6℃

T_m = 35.6℃

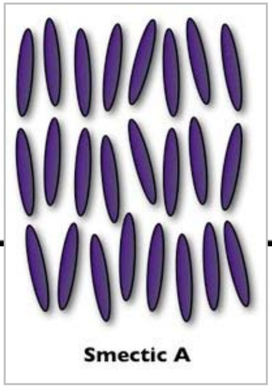


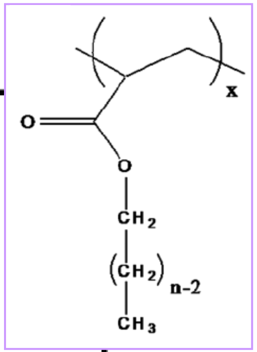
Soft-Matter Optical Spectroscopy

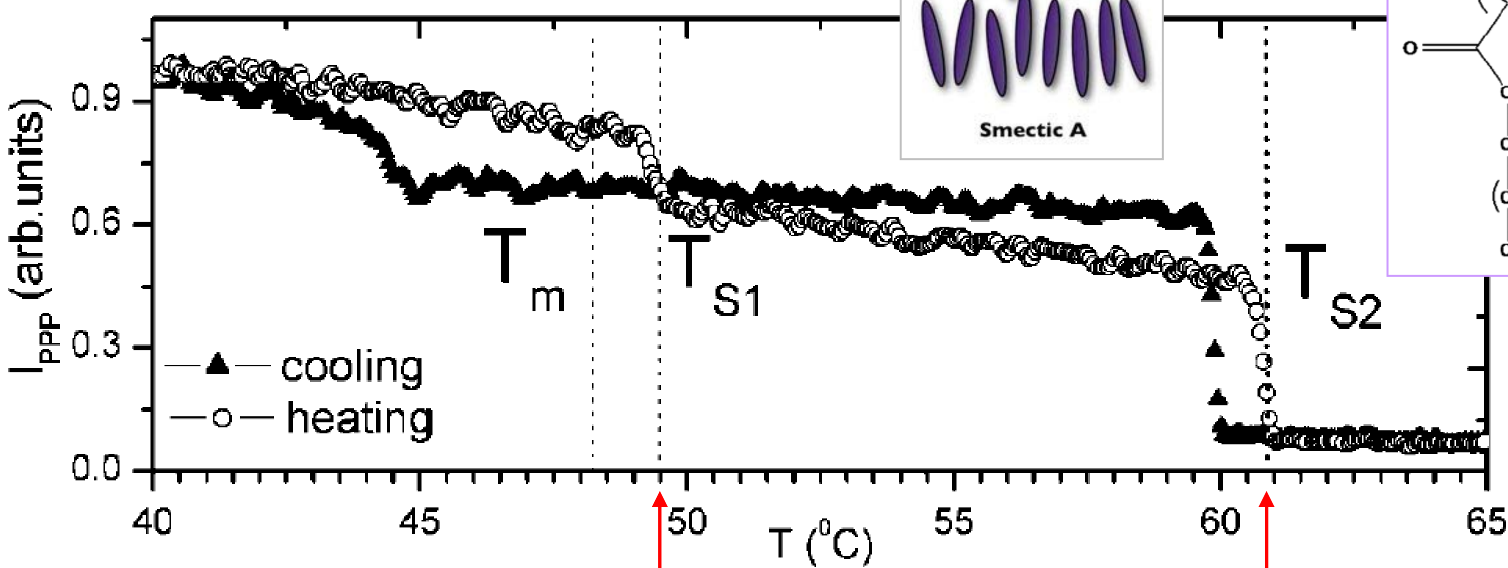
Introduction : Surface freezing of polymer

A. Dhinojwala and coworkers, Phys. Rev. Lett., **88**, 145501 (2002)

order-to-disorder <u>transition</u> : in two steps
(crystal --- hexatic smecticlike --- disorder)







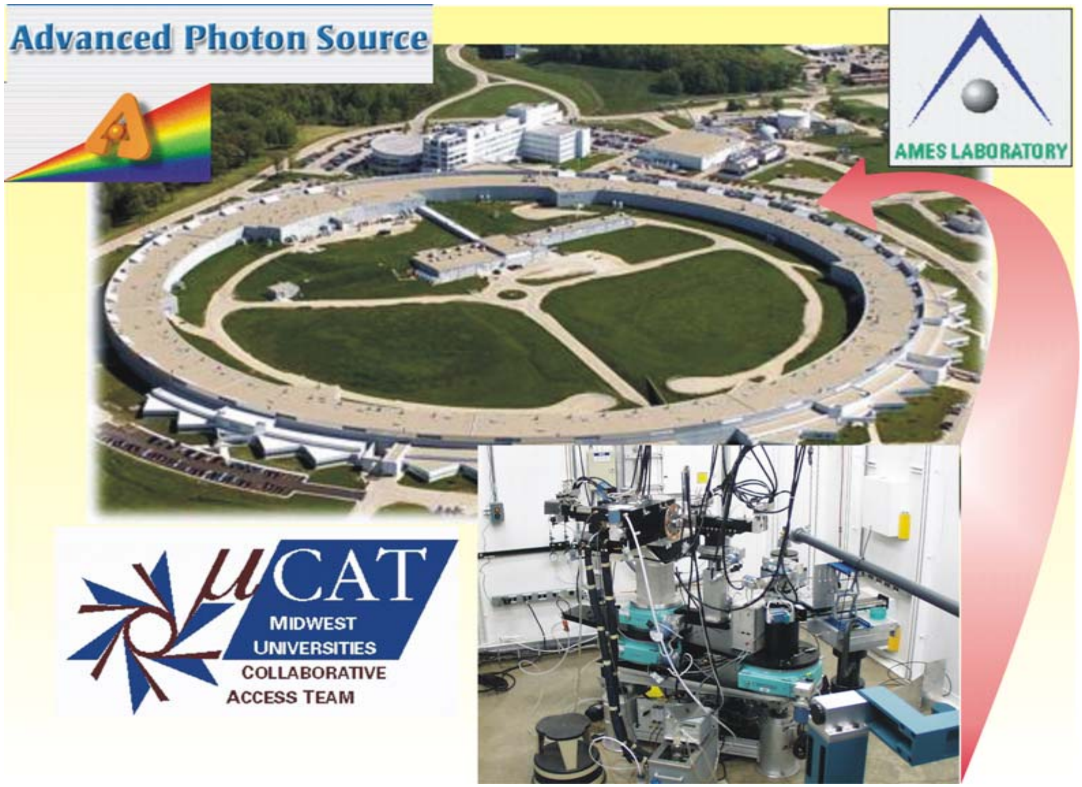
n	T_{S_1}(°C) Heat	T_{S_1}(°C) Cool	T_{S_2}(°C) Heat	T_{S_2}(°C) Cool	T_m(°C)
12	...	...	19.9 ± 0.3	18.6 ± 0.3	0
16	37.1 ± 0.3	33.3 ± 1.0	50.4 ± 0.3	48.6 ± 0.7	35.2
18	49.4 ± 0.1	44.2 ± 0.3	60.7 ± 0.1	59.6 ± 0.5	48.2
22	66.4 ± 0.1	61.4	75.7 ± 0.1	74.5	65.3

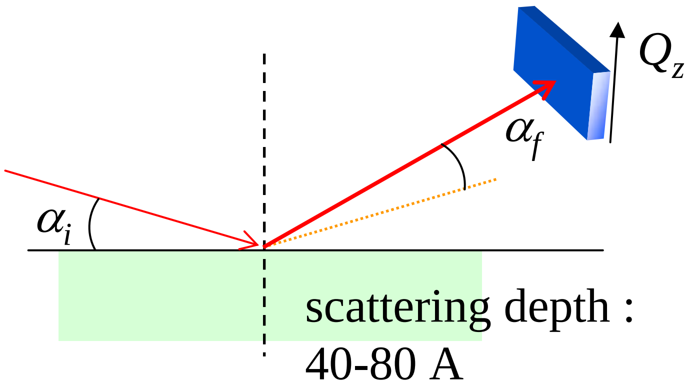
1-2 °C above the T_m

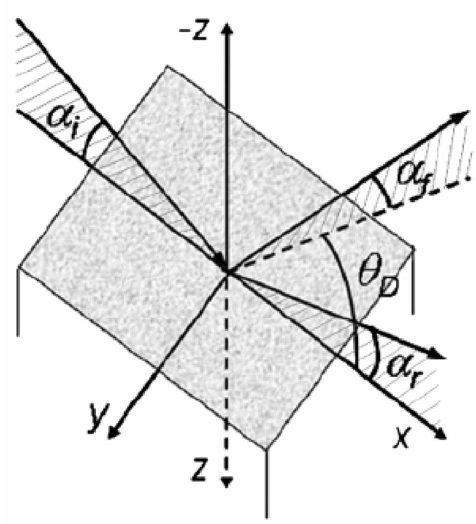
10-20 °C above the T_m

Soft-Matter Optical Spectroscopy

Experiment : X-ray scattered diffraction (GIXD) & Reflectometry







Observation of Novel Liquid-Crystalline Phase above the Bulk-Melting Temperature

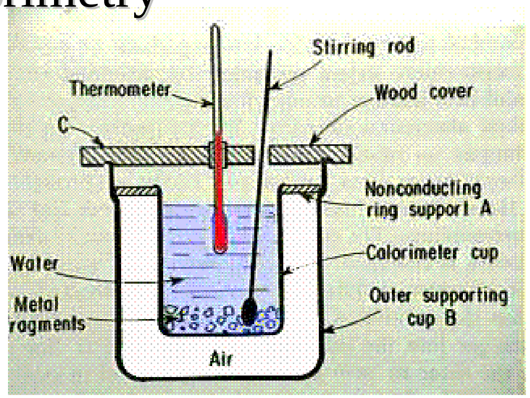
Phys. Rev. Lett. ***90****, 215501 (2003)*

In this paper, we show that a noncrystalline but ordered smectic-like phase exists above the bulk-melting temperature (T_m) at poly(n-alkyl acrylates)-air interface. The surface ordered phase is one monolayer thick and undergoes a sharp transition from order to disorder 10 °C above T_m for $n = 22$. The presence of a surface phase that does not exist in the bulk has important implications in the design of thermally responsive adhesives.

Soft-Matter Optical Spectroscopy

Previous studies : bulk properties of poly comb polymer

Calorimetry

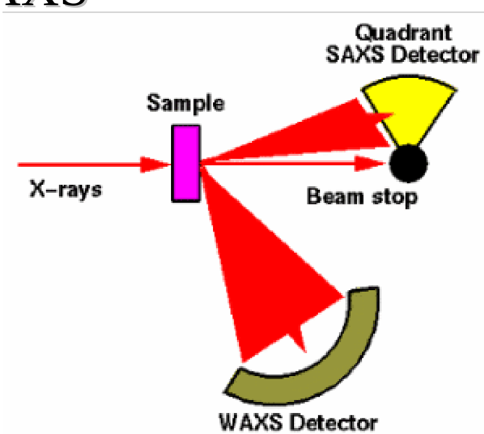


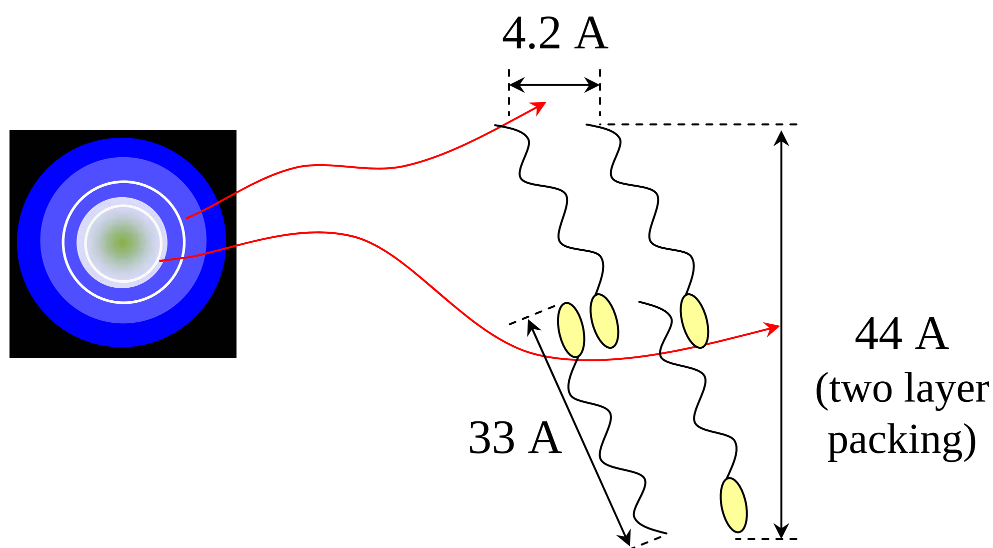
cooling rate : 0.3 °C/min

n	T_{S_1}(°C) Heat	T_{S_1}(°C) Cool	T_{S_2}(°C) Heat	T_{S_2}(°C) Cool	T_m(°C)
12	...	...	19.9 ± 0.3	18.6 ± 0.3	0
16	37.1 ± 0.3	33.3 ± 1.0	50.4 ± 0.3	48.6 ± 0.7	35.2
18	49.4 ± 0.1	44.2 ± 0.3	60.7 ± 0.1	59.6 ± 0.5	48.2
22	66.4 ± 0.1	61.4	75.7 ± 0.1	74.5	65.3

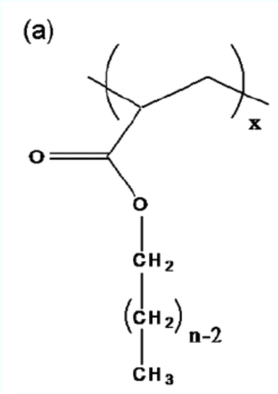
A. Dhinojwala and coworkers, Phys. Rev. Lett., **88**, 145501 (2002)

WAXS

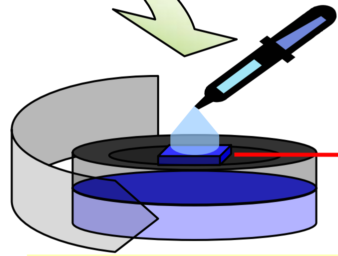




Sample preparation : spin coating



2-4 wt % solution in toluene



glass substrate

spin coating

thickness : 100-150 nm

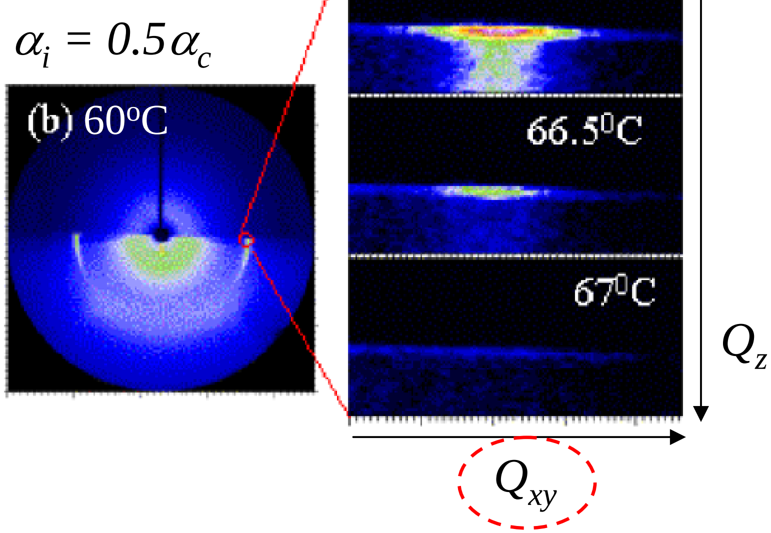
T_a : T_m + 10 (or 20) ^{o}C for 4-5 h

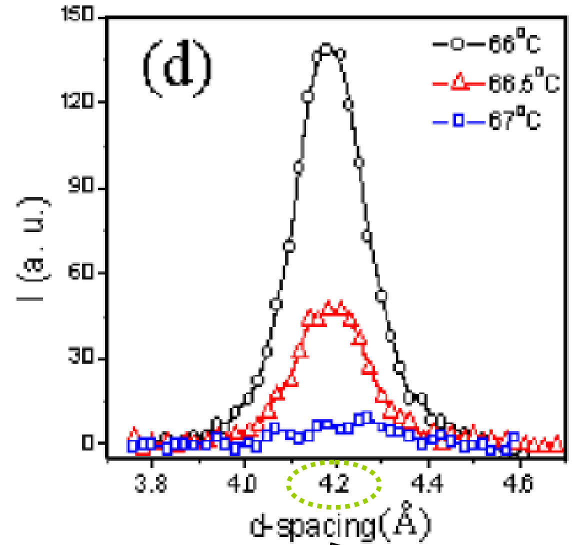
annealing

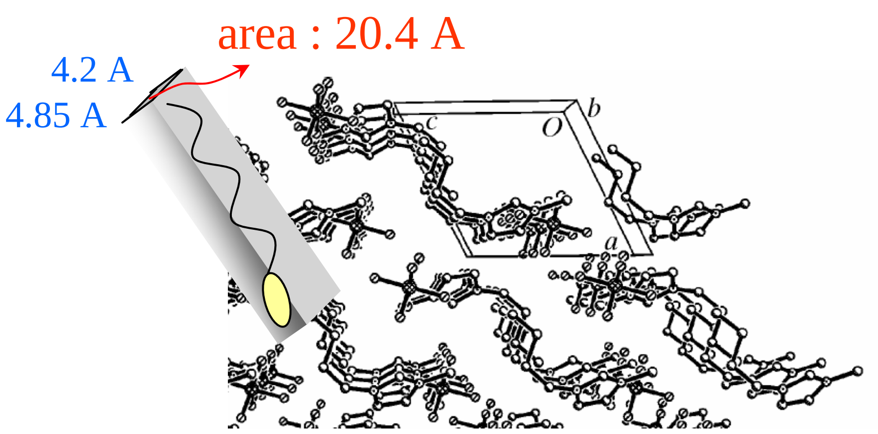
Surface measurement

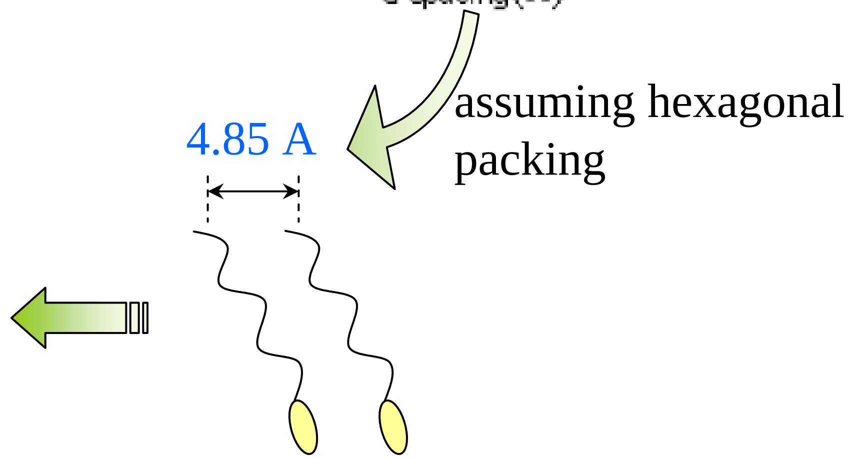
In-plane lattice spacing

* T_m = 64.9 °C

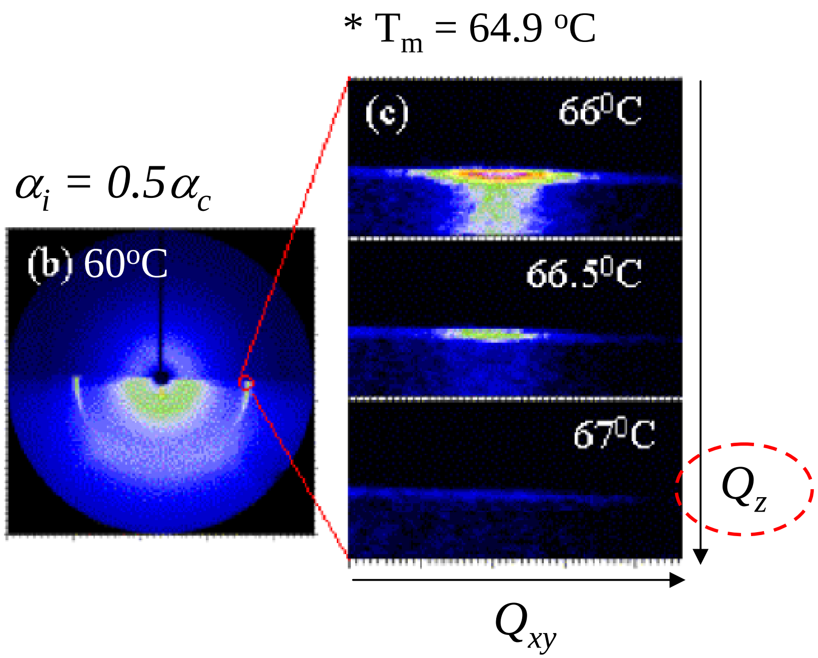


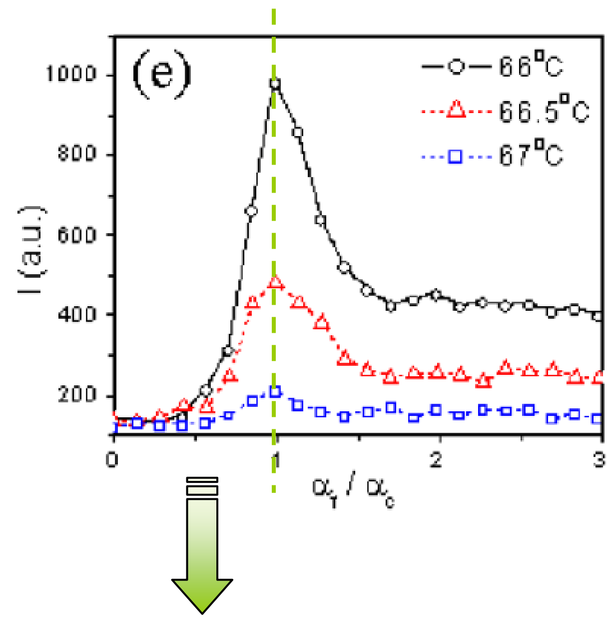






Melting transition : scattering depth

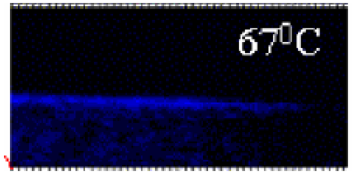




scattering depth : ~40 A

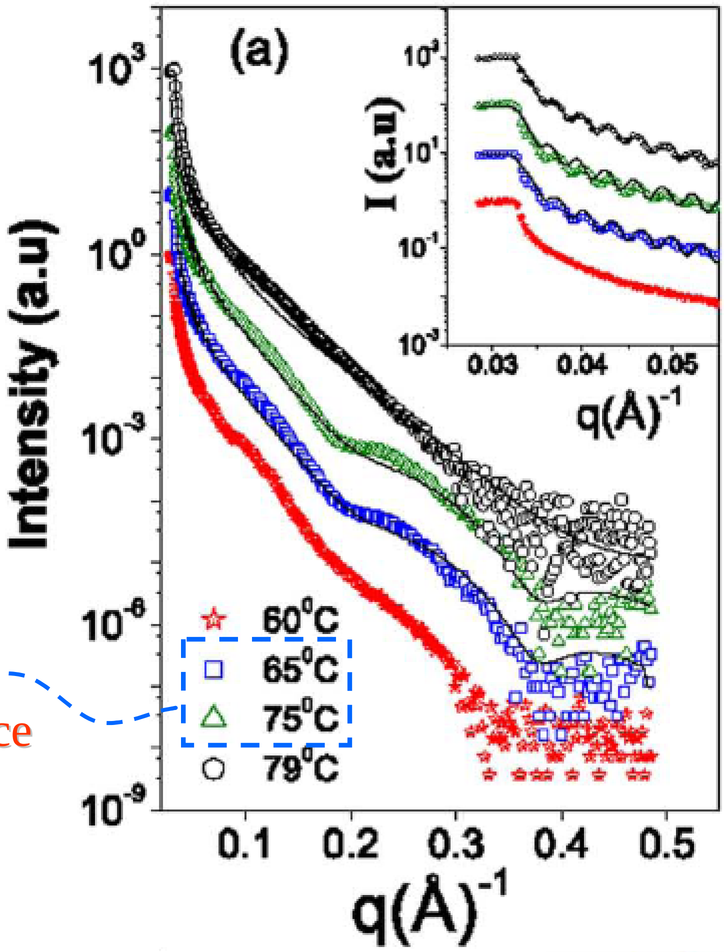
Temp. dependant surface layering

long-range crystalline order

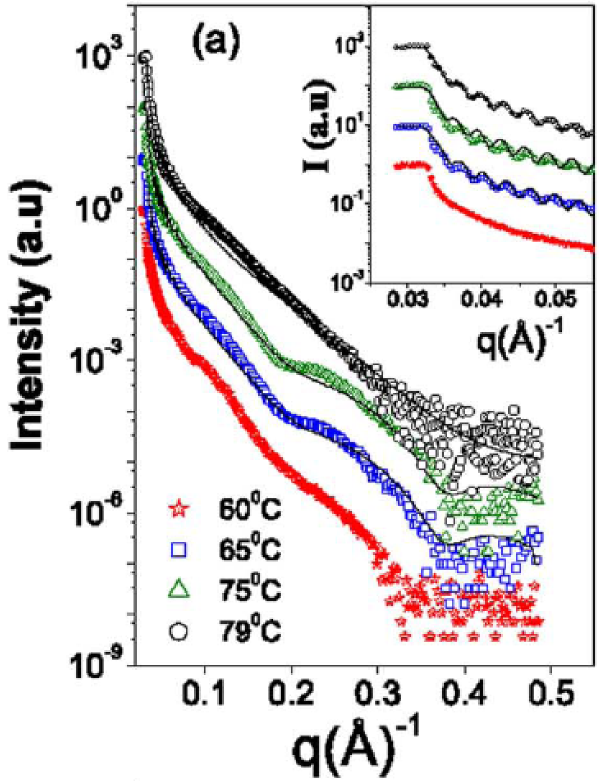


GIXD : lost

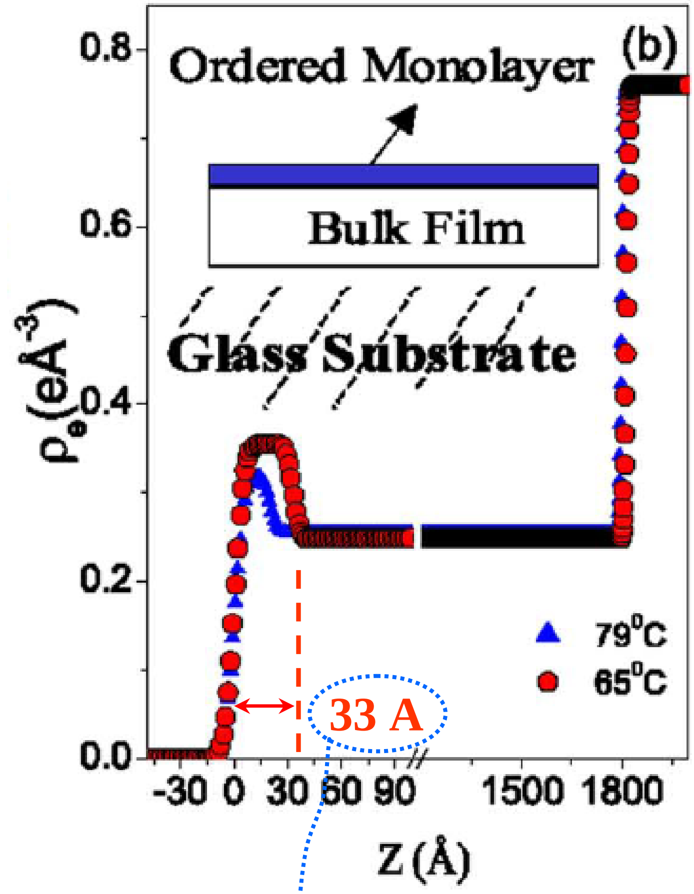
XR : presence



Temp. dependant surface layering



solid lines : two-layer model



monolayer of a predominantly **trans**-alkyl side chain

Partial Crystallinity in Alkyl Side Chain Polymers Dictates Surface Freezing

Phys. Rev. Lett. ***101****, 065505 (2008)*

We have studied the structure of a novel crystalline surface monolayer on top of a disordered melt of the same material [poly(*n*-alkyl acrylate)s] using grazing incidence x-ray diffraction. The grazing incidence x-ray diffraction, surface tension, and bulk latent heat results show that side chains crystallize except the nine methylene units of the alkyl side chains closest to the polymer backbone. The partial crystallinity along with a thicker surface layer, due to the additional length of the linker group, explains why the difference between the surface order-to-disorder transition temperature and bulk melting temperature increases with a decrease in the length of the alkyl side chain.

Soft-Matter Optical Spectroscopy

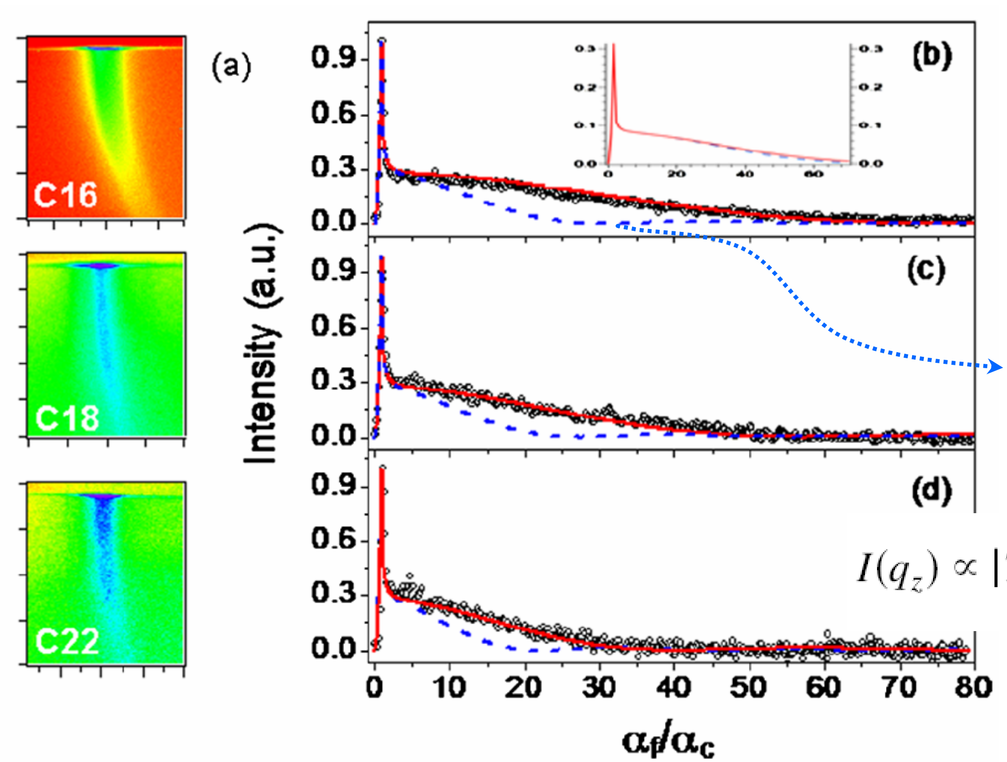
Theory : intensity of scattered wave

$$I(q_z) \propto \left|T(\alpha_i)\right|^2 \left|T(\alpha_f)\right|^2 \left[\left(\frac{\sin(q_z D/2)}{q_z D/2}\right)^2\right]$$

- $T(\alpha_i)$: Fresnel coefficient of the incident field
- $T(\alpha_f)$: Fresnel coefficient of the reflected field
- D : length of crystal structure normal to the surface

$d\gamma / dT$: **difference** in bulk and surface **entropy**

Partial crystallinity



dashed :
D = extended side chain length

$$I(q_z) \propto |T(\alpha_i)|^2 |T(\alpha_f)|^2 \left[\left(\frac{\sin(Q_z D/2)}{Q_z D/2} \right)^2 \right]$$

partial crystallinity of the side chains

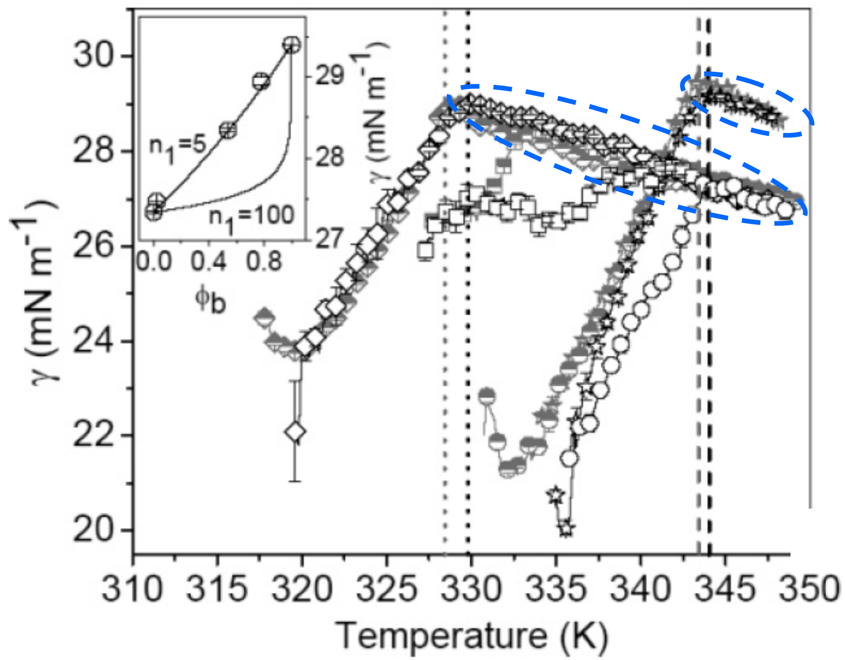
T_m	T_{s2}
308.2 K	320.0 K
320.7 K	329.8 K
336.5 K	344.0 K

Polymer, *n*	*D* (Å)	All-*trans* side chain length (Å)	x_{GIXD}
16	7.9	19.3	9.0
18	10.5	21.9	8.9
22	15.0	26.9	9.4

Soft-Matter Optical Spectroscopy

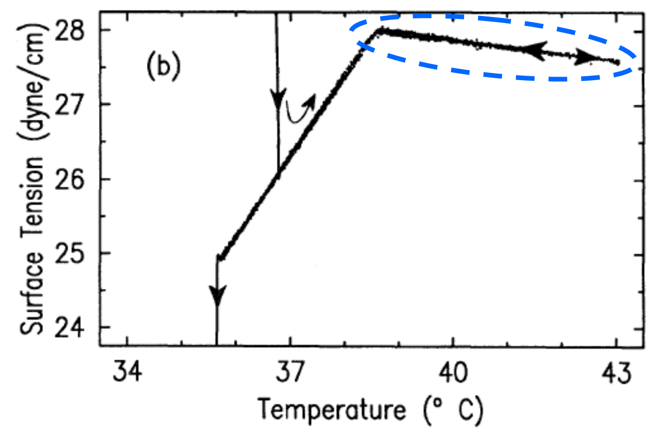
Surface tension

$(d\gamma / dT)_{T>Ts2} \sim -0.11$ mN/m · K^{-1}



A. Dhinojwala and coworkers, Mactromolecules., **38**, 2541 (2005)

$(d\gamma / dT)_{T>Ts2} \sim -0.09$ mN/m · K^{-1}



Phys. Rev. Lett, **70**, 958 (1993)

n	$\Delta\gamma$	$(d\gamma/dT)_{T<T_{s2}}$	$\Delta(d\gamma/dT)$	ΔS_b	$\Delta(d\gamma/dT)_{calc}$
16	4.6	0.46	0.59	0.51	0.52
18	5.1	0.57	0.68	0.64	0.67
22	6.6	0.89	0.98	0.88	0.97

calculation with $x_{GIXD} = 9$

* ΔS_b : calculated using bulk DSC measurements

Soft-Matter Optical Spectroscopy