Neutron Scattering for Polymer R&D in the Petrochemical Industry

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Outline

- Overview of Polymer R&D in the Petrochemical Industry
  - Polyethylene (PE), Polypropylene (PP)
    - World consumption, Markets, Products
  - Polyesters (e.g PET), Polyethylene glycol (PEG)
- Microstructure of Semi-crystalline Polymers
  - Inter-crystalline Connectivity Dictate Mechanical Performance
    - Understanding tie chains and branching in PE
  - The “Shish-Kebab” Morphology of Polyolefins
    - SANS as a tool to understand origin of molecular structure of PP
- Polymer Fractionation in Binary Solvents
  - Tools to Easily Separate Polymers by Molecular Weight
  - PEG has Different Chain Conformation in Different Solvents

Polymer R&D in the Petrochemical Industry

- Commodity Polymers
  - Polyethylene
    - Packaging, Building and Construction, Consumer
  - Polypropylene
    - Packaging, Non-wovens, Automotive Materials
  - Polyethylene Terephthalate
    - Bottles, Fleece Fibers
- Polymers as Additives
  - Polyethylene Glycol
    - Biotech, Nanotech, Personal Care Product Industry, Models for Complex Biomaterials

Crude Oil to Polymer Product

Crude Oil

Refinery

Steam Cracker
Naptha Cracker
FCC

Plastics plant

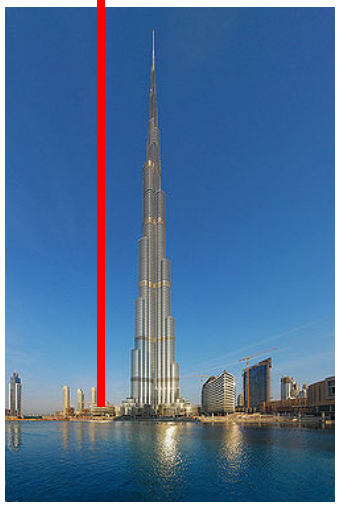
Pellets stored and shipped in hopper cars

Processing plants

Consumer products

Global Polyolefin Consumption

Current number = 200 Million Tonnes per Year



> 2 times as tall as the Burj Khalifa in Dubai (2174 m c.f. 828 m)

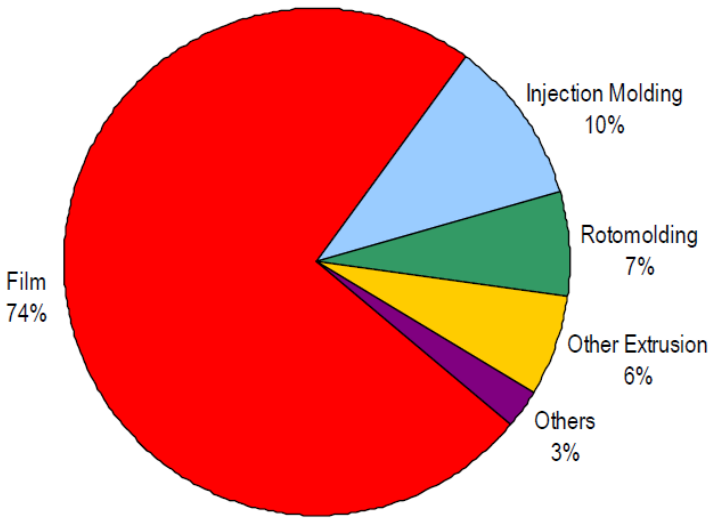
Half the weight of a person *per person, per year* (30.8 kg/person/yr)

425 μm film covering the earth

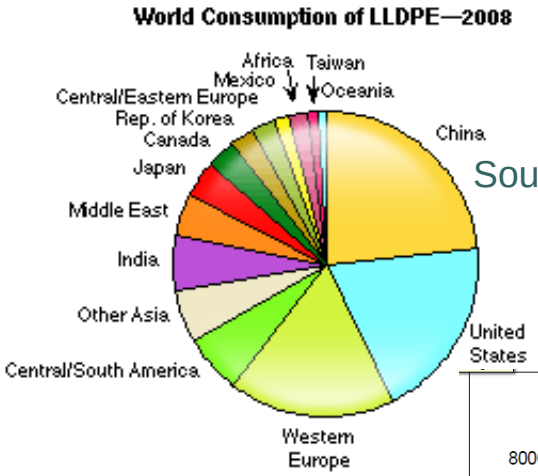
Polyethylene (PE)





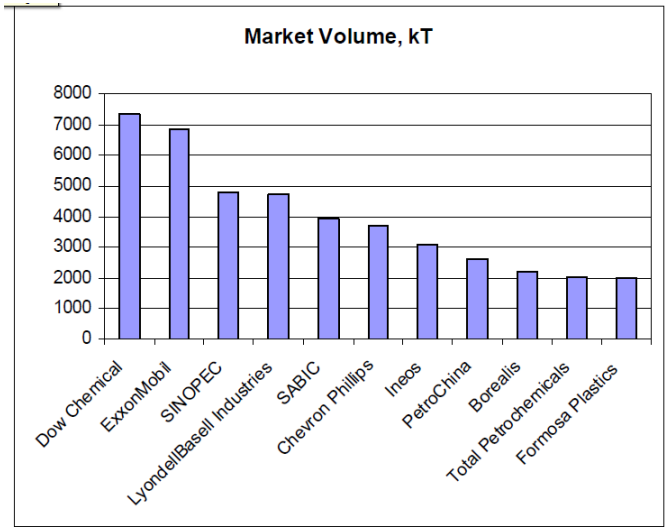



Source: Nexant/Chem Systems
PERP Report LLDPE 2008



Source: SRI Consulting

Source: Phillip Townsend

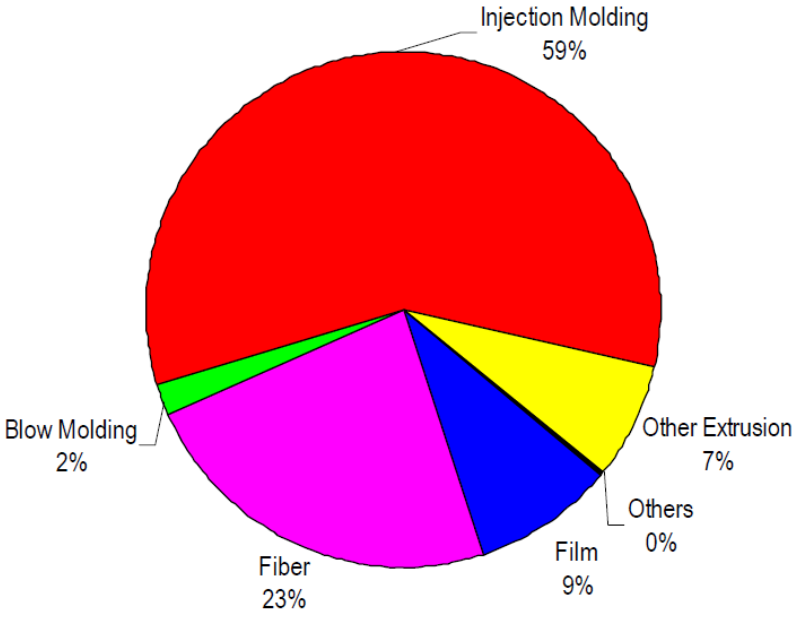


Polypropylene (PP)









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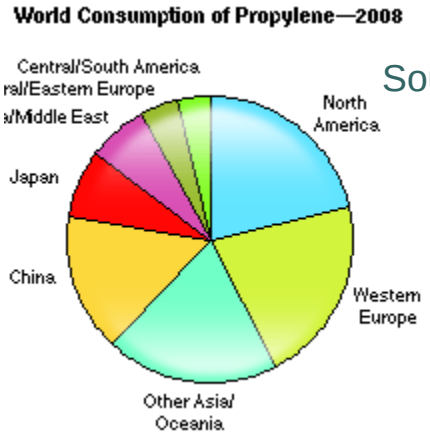
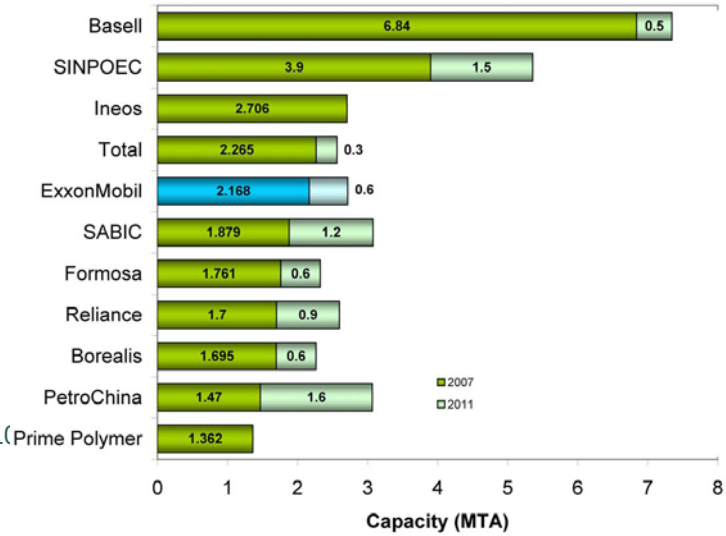
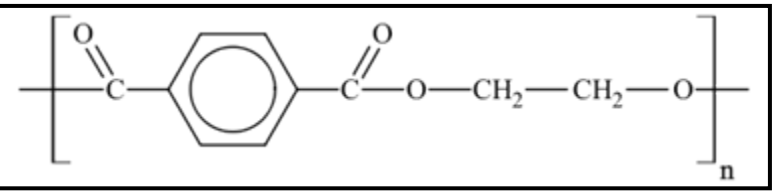


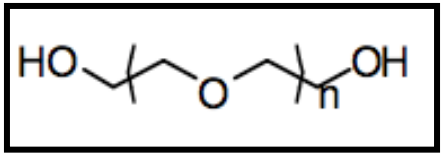
Source: SRI Consulting

Source: Lawson and Spiller,
ExxonMobil Chemical



Polyesters and Polyethers (PET and PEG)





- PET used in drinks bottles (excellent barrier materials)
- Recycled into PET fibers- clothing
- PET films market- protective covers for iPhones, TV dinners
- Largest market for PET in China

- PEG has a low toxicity, water-soluble and used in a variety in medical applications
- Used as a dispersant in toothpaste and skin creams
- PEG copolymers form micelles and vesicles- drug delivery.

Why Scattering in General for Polymer R&D?

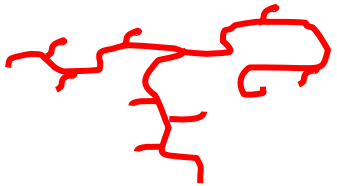
- Polymers often contain crystalline and non-crystalline domains (e.g. PE, PP, PET, PEG). These differences result in a periodic electron density profile and can be studied by x-ray scattering.
- SAXS/WAXS used for time-resolved studies such as crystallization, stretching experiments…faster than SANS
- SANS: doesn't measure change in electron density but changes in scattering length density, can either:
  - Deuterate the solvents and look at polymer chain structure (difficult by SAXS- not as large a change in electron density between solvent and polymer chain)
  - Selectively deuterate the chain and look at parts of the chain, unlike SAXS

Microstructure of Semi-crystalline Polyolefins

No branching

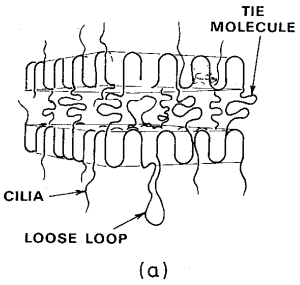
Short chain branching

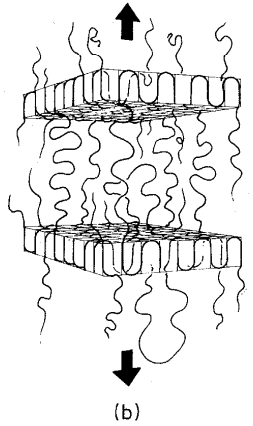
(SCB)

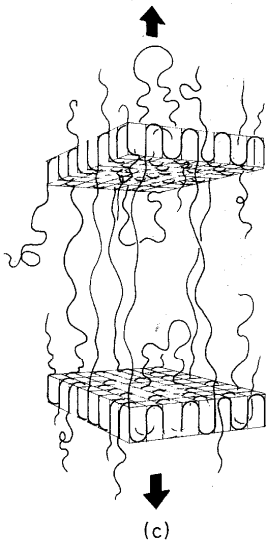


Long and short chain branching

(LCB + SCB)







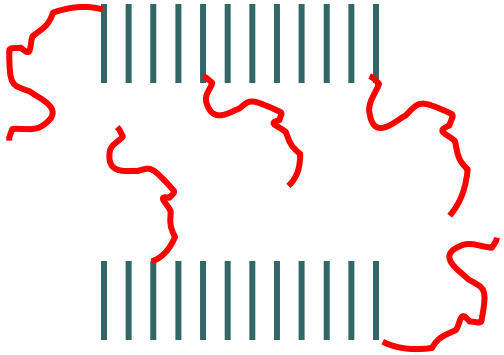
Crystals stack into (often oriented) arrays separated by amorphous non-crystalline regions.

Amorphous regions give strength and the ability to stretch to the material

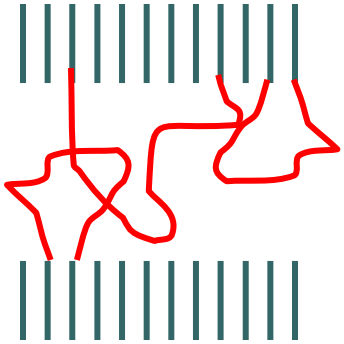
Tie chains

- **No branching- long crystals form**
- **SCB – Short branches (from the comonomer: butene, hexene or octene) prevent part of the chain from entering the chain folded crystal regime. SCB poisons the crystallization. These amorphous chains can do one of three things:**

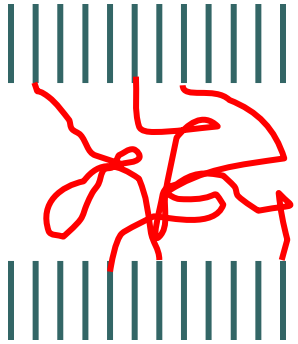
Dangle off the chain ends



Loop back into the same crystal



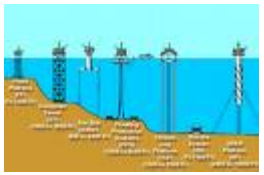
Tie 2 or more crystals together



<u>Tie chains span more than one crystalline region and are what provide PE, PP with their strength, impact resistance and toughness.</u>

<u>Crystal regions act as anchors for neighboring tie chains.</u>

An example of the importance of tie chains



Water-injection flow lines used in offshore oil industry.

High temperatures routinely used to preserve the reservoir pressure and allow economic extraction of oil from its source.

H_2S can form which corrodes metal flow lines. Huge cost disadvantage and lower lifetime of well.

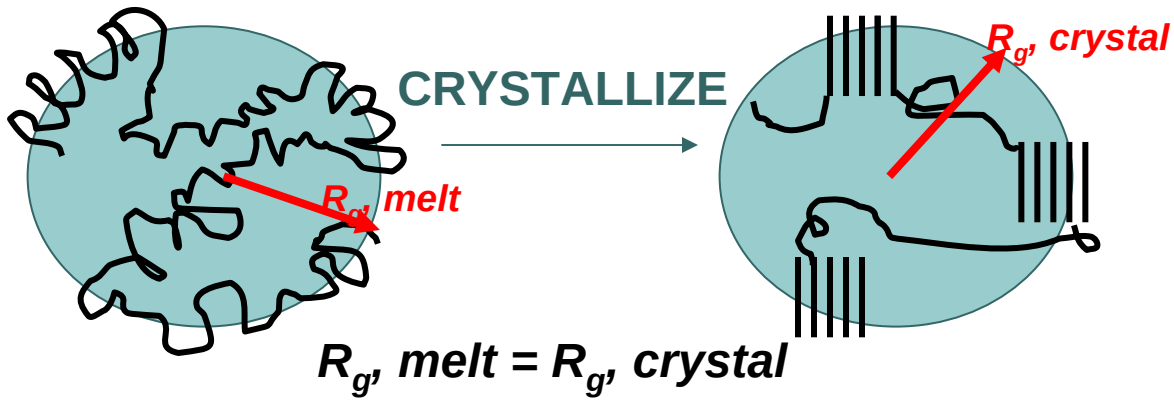
<u>Use Plastic Pipes:</u>

HDPE has great strength at elevated temperatures but limited long term creep. Reduce the density, but this results in lower heat stability.

High tie chain concentration of lower density PE. Provides pipes with long term hydrostatic strength with excellent flexibility (easy to mold).

<u>BY CONTROLLING THE COMONOMER DISTRIBUTION WE CONTROL THE TIE CHAINS AND DICTATE MECHANICAL PROPERTIES</u>

Measurement of Tie Chains



R_g of the molecule is greater than the lamellae thickness, so assume that one molecule spans more than one lamellae

Fisher model calculates tie chains without taking onto account chain re-entry.

Various lamellae exist as clusters or crystal stems that are connected by folded chains.

The clusters scatter as independent units over a given size range. This scattering is dependent on the number of stems per cluster, N_c.

Measurement of Tie Chains

$$\frac{1}{I(q)} = \frac{1}{N_s}\left[1 + \frac{1}{3}q^2 R_g{}^2\right]$$

Number of stems per molecule at small *q*

$$\frac{1}{I(q)} = \frac{1}{N_C + 1}\left[1 + \frac{N_C}{2(N_C - 1)}q^2 R_g{}^2\right]$$

Number of stems per cluster at intermediate *q*

$$\upsilon = N_s / N_C$$

Number of clusters per molecule

$$\upsilon - 1$$

Minimum number of tie chains

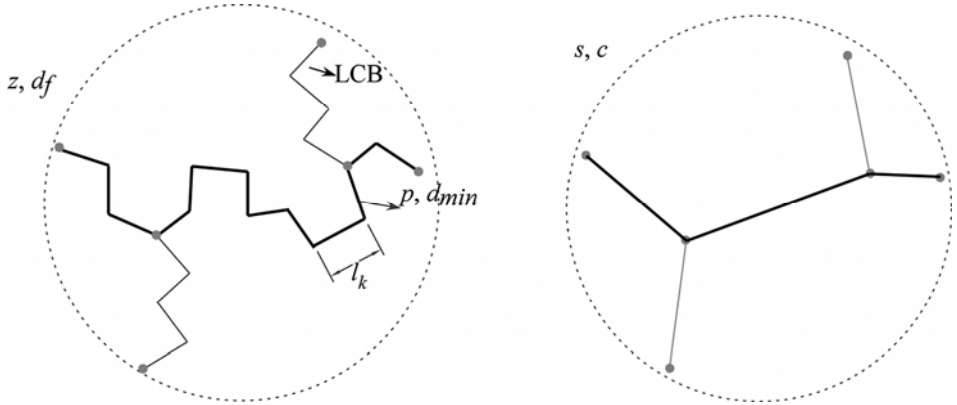
$$P(t) = (\upsilon - 1) \times 100 / N_C$$

Probability of tie chains (%)

Estimation of Degree of Branching in Non-Deuterated Polymers

Hydrogenated polymers in deuterated solvent: easy, cheap.

Investigates LCB content of PE



Dark lines = average minimum path for linear chain

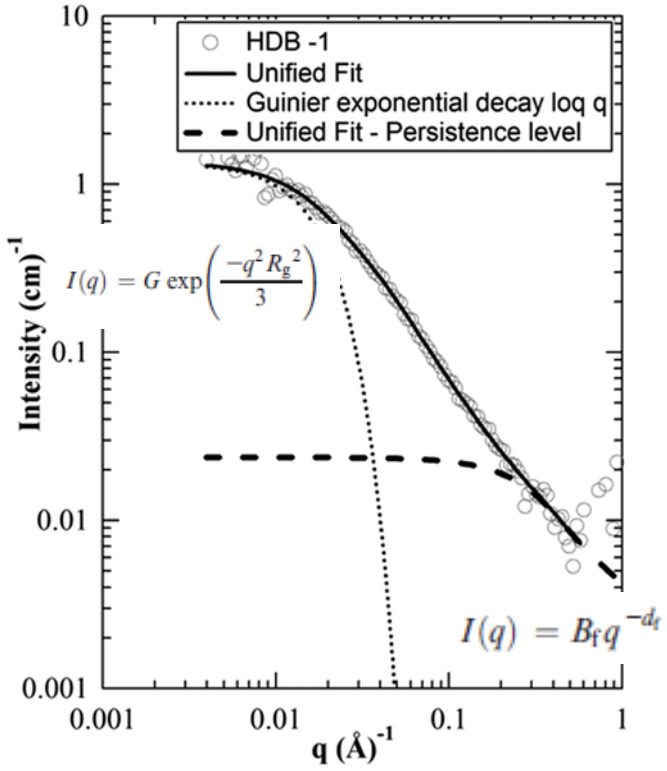
Light lines = Long chain branch (LCB)

GPC – ineffective in characterizing LCB

NMR – cannot see differences in SCB + LCB

Rheology – semi-empirical and qualitative

Unified Model Quantifies LCB in Polyethylene



$$I(q) = \{G_2 e^{-(q^2 R_{g2}{}^2)/3} + B_2 e^{-(q^2 R_{g1}{}^2)/3}(q_2^*)^{-d_{f2}}\}$$

$$+ \{G_1 e^{-(q^2 R_{g1}{}^2)/3} + B_1 (q_1^*)^{-1}\}$$

$$\phi_{br} = \frac{z-p}{z} = 1 - z^{(1/c)-1}$$

$$d_{min} = \frac{B_f R_{g,2}^{d_f}}{C_p \Gamma\left(\frac{d_f}{2}\right) G}$$

for $1 \le d_f < 3$

p = minimum path in Kuhn steps

c = connectivity dimension

z = chain length

d_{min} = average minimum path dimension

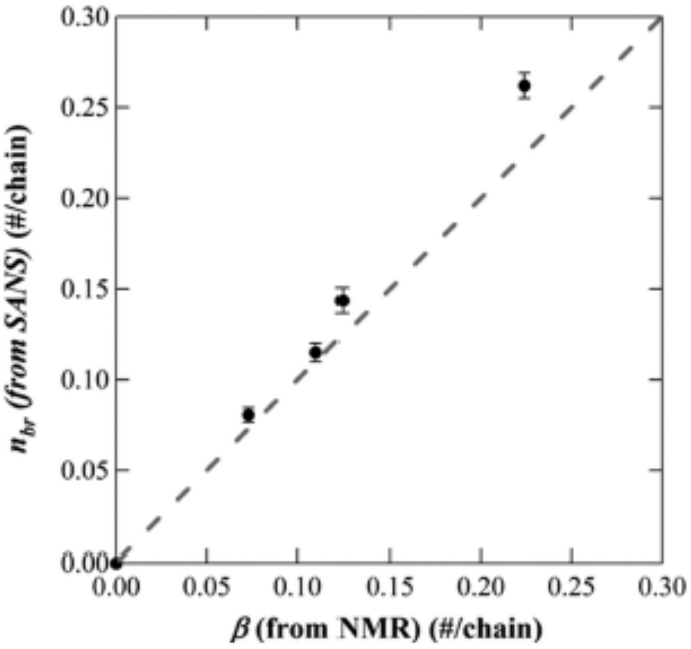
Bf, G = scaling prefactors

Novel scaling approach (combination of Guinier decay and mass fractal scaling) determines mole fraction of LCB, number of LCB and average branch length

LCB Quantification

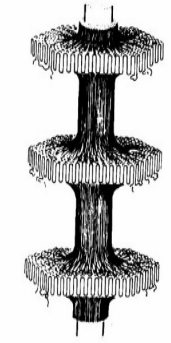
sample	LCB/10^3C ^{13}C NMR[a]	M_n (g/mol)[a]	PDI (M_w/M_n)[a]	β	n_{br}	$n_{br,p}$	ϕ_{br}	z_{br} (g/mol)
HDB-1	0.026	39 300	1.98	0.073	0.080 ± 0.004	0.047 ± 0.005	0.10 ± 0.02	$12\,700 \pm 1500$
HDB-2	0.037	41 500	1.93	0.110	0.115 ± 0.005	0.053 ± 0.005	0.14 ± 0.02	$17\,400 \pm 1600$
HDB-3	0.042	41 200	1.99	0.124	0.144 ± 0.007	0.065 ± 0.005	0.17 ± 0.02	$16\,500 \pm 1600$
HDB-4	0.080	39 200	2.14	0.224	0.262 ± 0.007	0.090 ± 0.008	0.28 ± 0.03	$18\,600 \pm 1700$

Excellent agreement with NMR



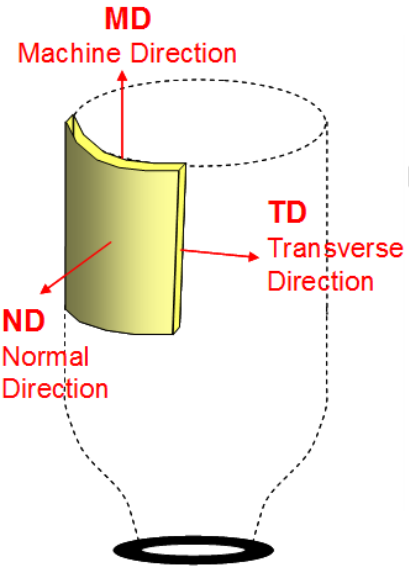
This scaling law also been used to determine branch content of ceramic aggregates (Beaucage 2004) and degree of folding in proteins and RNA (Beaucage 2008)

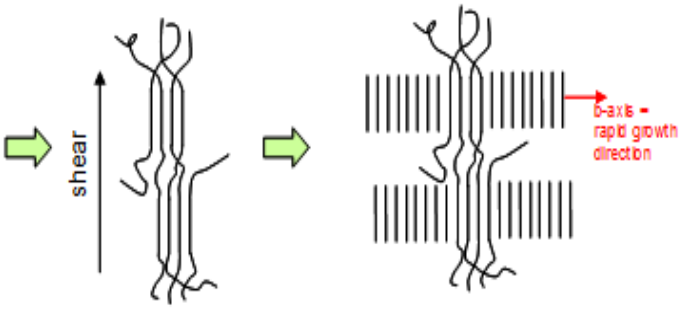
Microstructure of Semi-crystalline Polyolefins

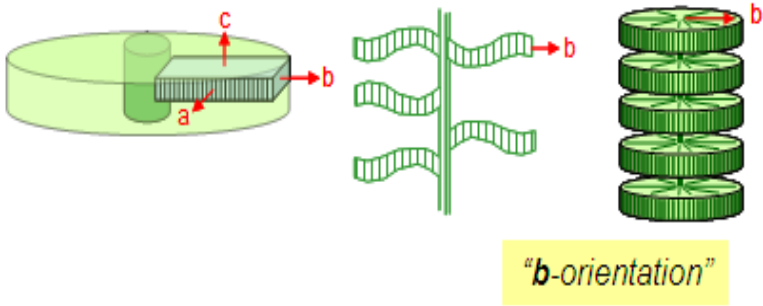


Industrially, polymers are not crystallized slowly from the melt.

They are rapidly crystallized under shear flow: fiber spun, extruded, cast films, **biaxially stretched blown films**.







*"**b**-orientation"*

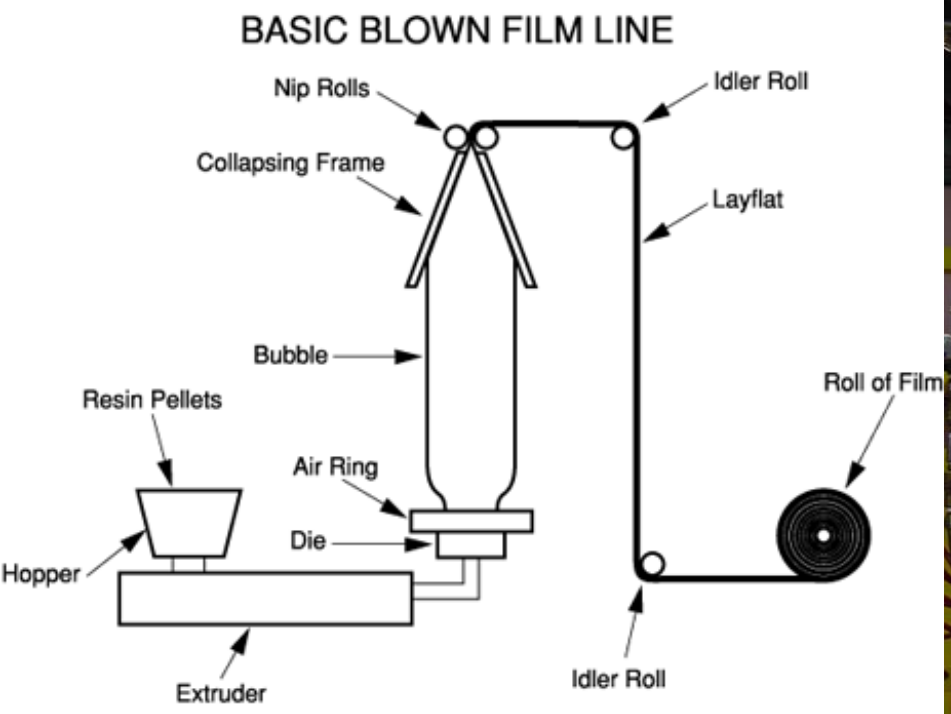
Diagram courtesy of A.J.Bons, private communication

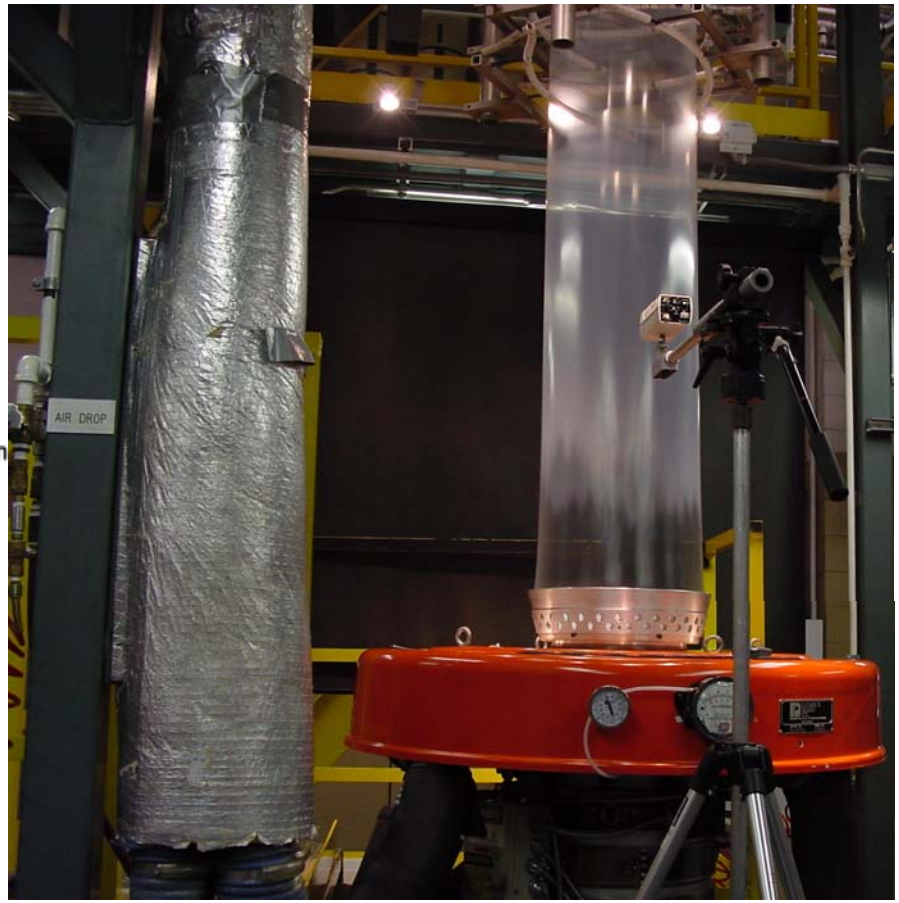
Chains in the melt order in the processing direction.

Crystals nucleate from this central ordered melt phase and grow perpendicular to the processing direction. These lamellae stock to form a **row-nucleated structure, or "Shish-Kebab Morphology"**

Which chains go where??

Blown Film Line: Polyethylene

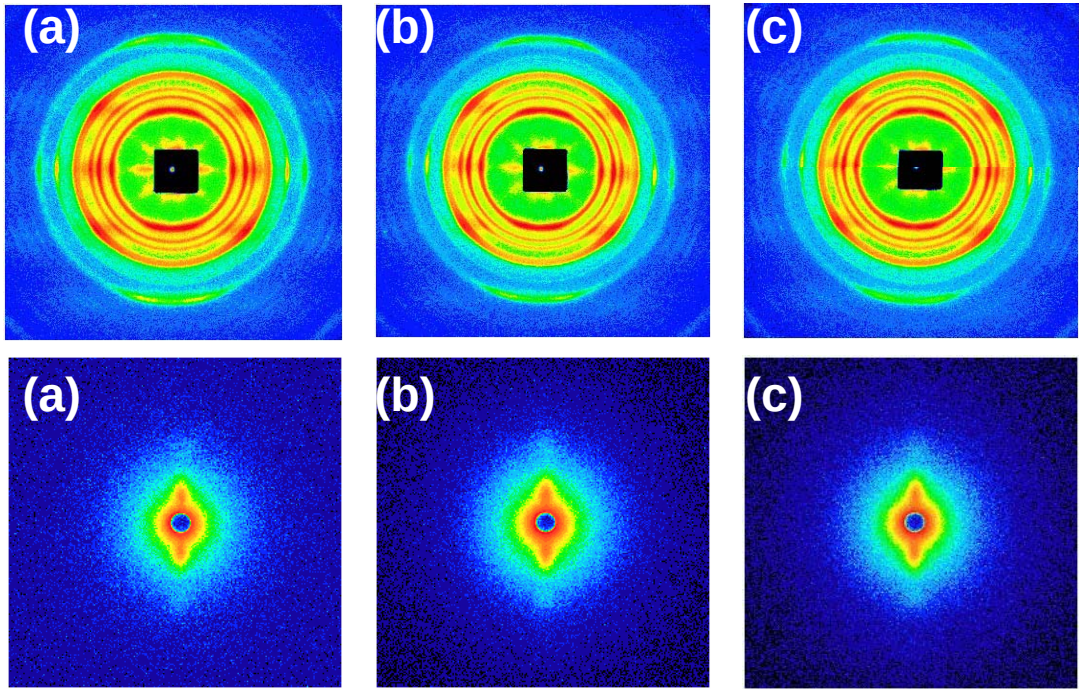




Molecular Origin of Shish-Kebab Morphology

WAXS

SAXS

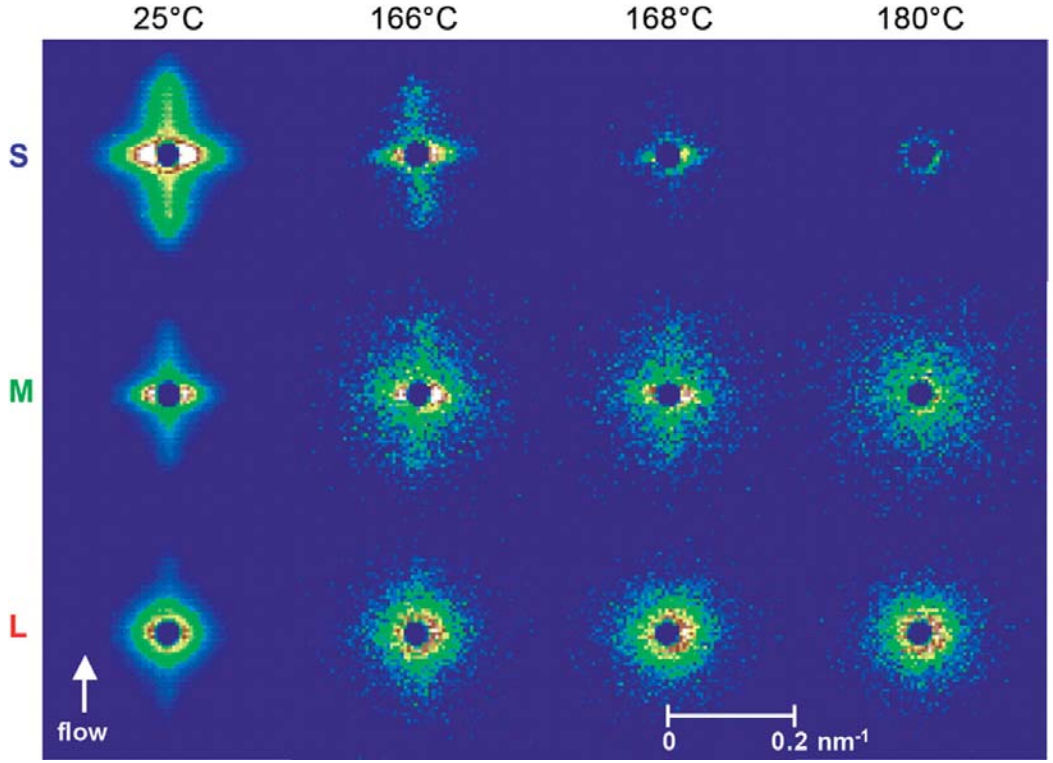


Science 18 May 2007: Vol. 316. no. 5827, pp. 1014 - 1017

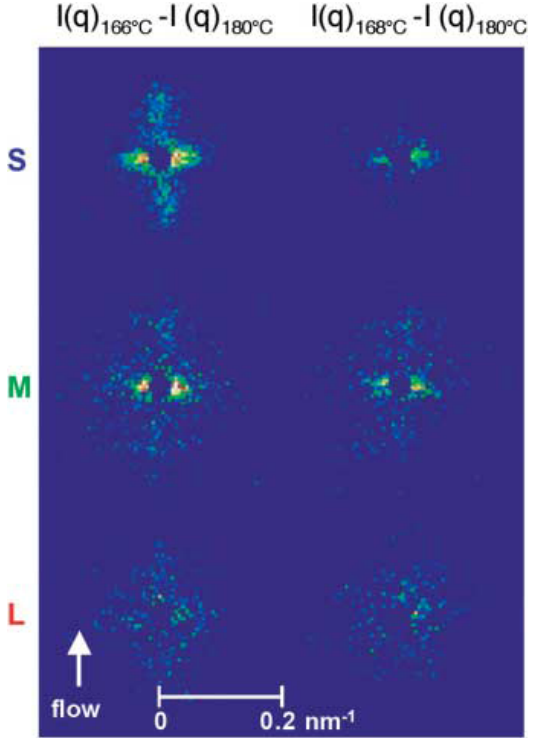
No differences in SAXS/WAXS from iPP samples which have either:
(a) short (~ 40K), (b) medium (~ 200K) or (c) long (> 10^6 K) chains labeled with D

SANS Reveal Short, Medium and Long Chains all Persist in the Shish

Science 18 May 2007: Vol. 316. no. 5827, pp. 1014 - 1017

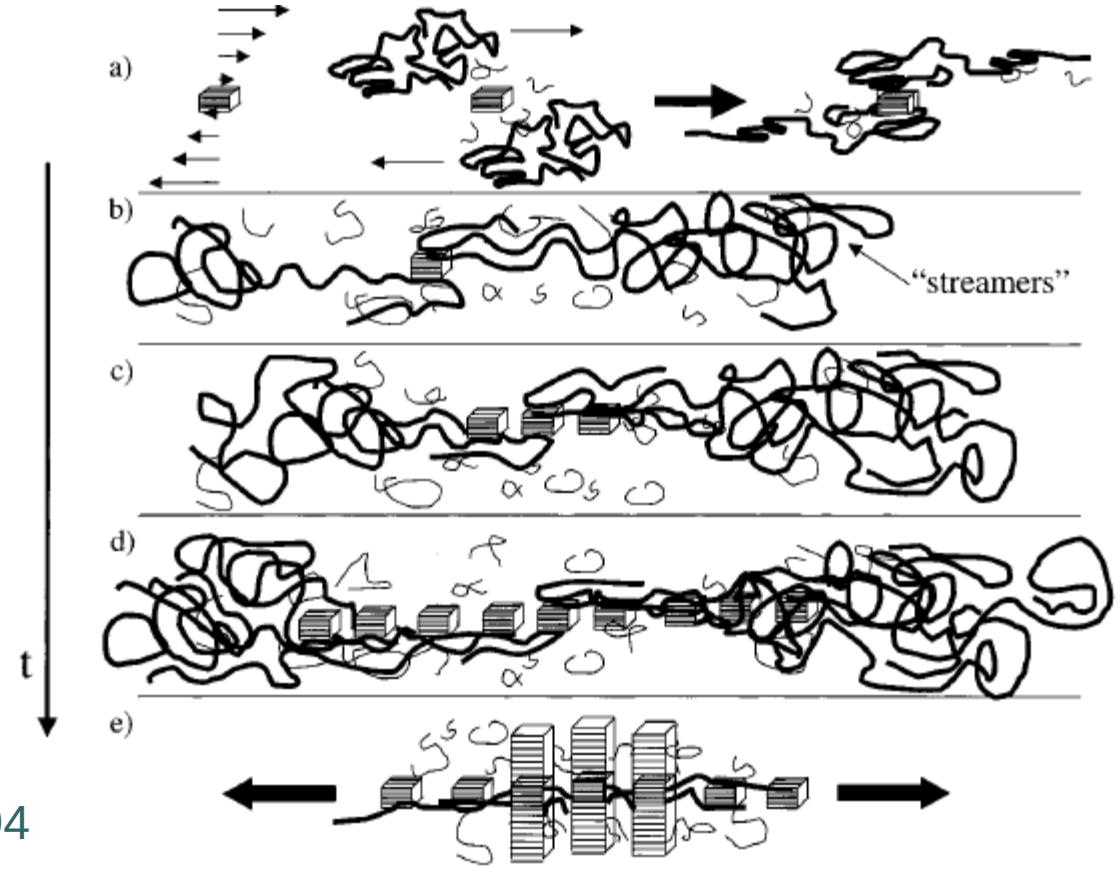


Crystalline lamellae for all chain lengths but less in medium and long chains- trapped in amorphous phase as **tie chains**



No Shish seen in long chains. Shish contain all chain lengths but long chains less oriented and “reel in” shorter chains which become more oriented

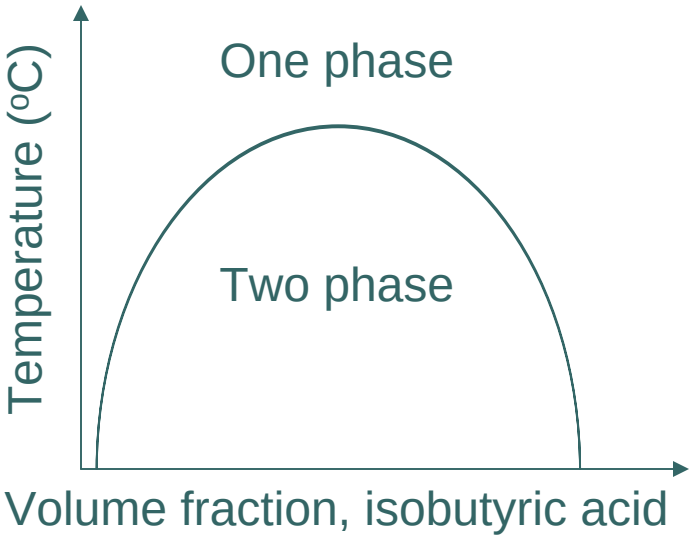
Mechanism of Shish Formation

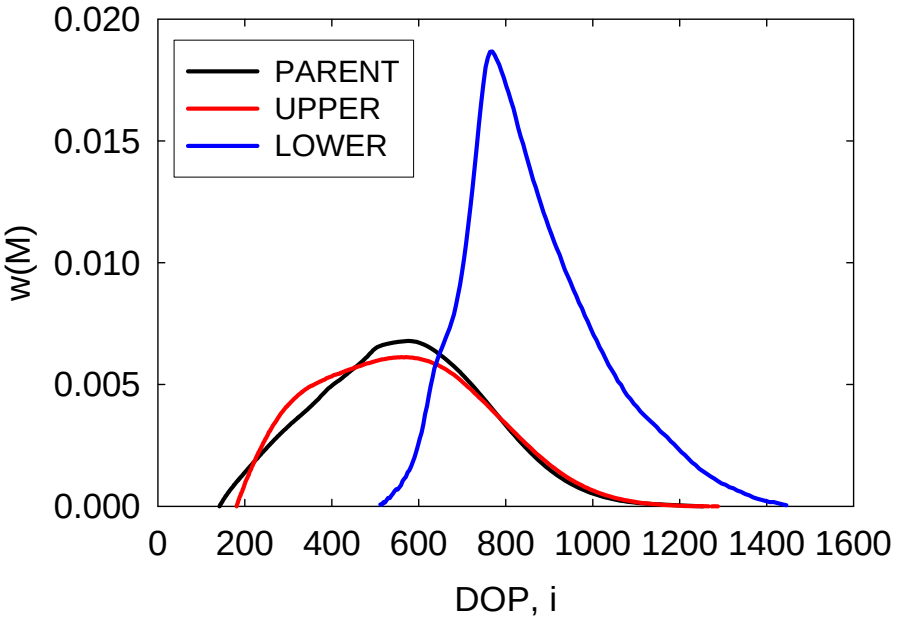


Macromolecules, **2002**, *35*, 2583-2594

Figure 13. Schematic diagram of the nature of shear induced nucleation and subsequent growth of oriented crystalline lamellae during short-term shearing above the threshold shear stress. (a) A long chain (bold line) dispersed in short chains in a supercooled polymer melt adsorbs to an existing pointlike precursor as it flows past. Dangling segments of adsorbed chains become oriented due to sustained shear. (b) Additional chains adsorb and their dangling segments form "streamers" upstream and downstream of the pointlike precursor. (c) The increased local orientation of the chain segments increases the probability that long-lived ordered structures will form. (d) More chains adsorb to these new nucleation sites and the process propagates a string of nuclei along the line of flow. (e) The nuclei along this thread lead to lateral lamellar growth.

Polymer Fractionation in Binary Solvents: PEG in Isobutyric acid + Water





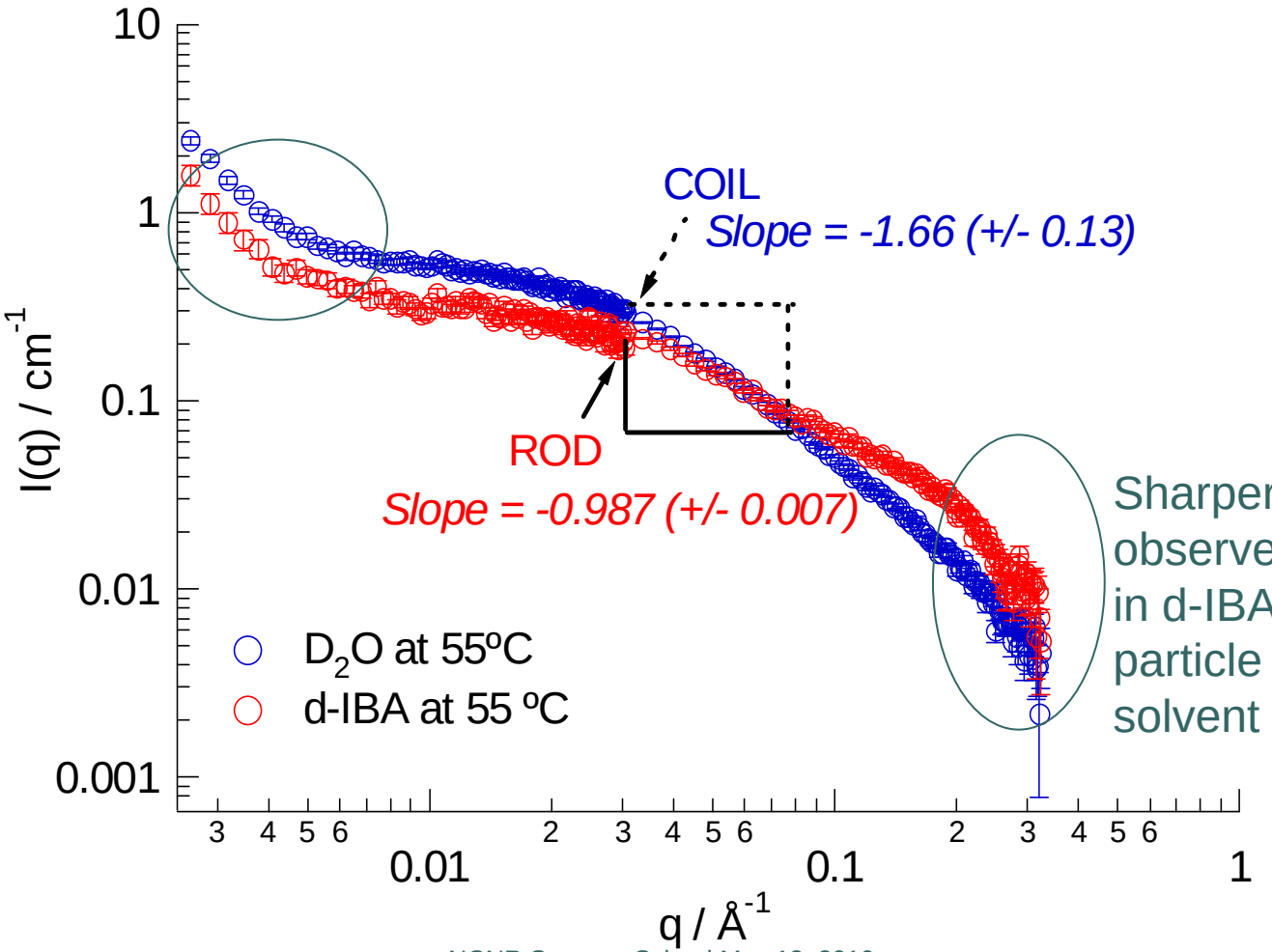
PEG added to a binary mixture of IBA and H_2O.

Heated above criticality and cooled to 2 phase region.

Each phase (upper IBA-rich and lower H2O-rich) assessed for PEG content

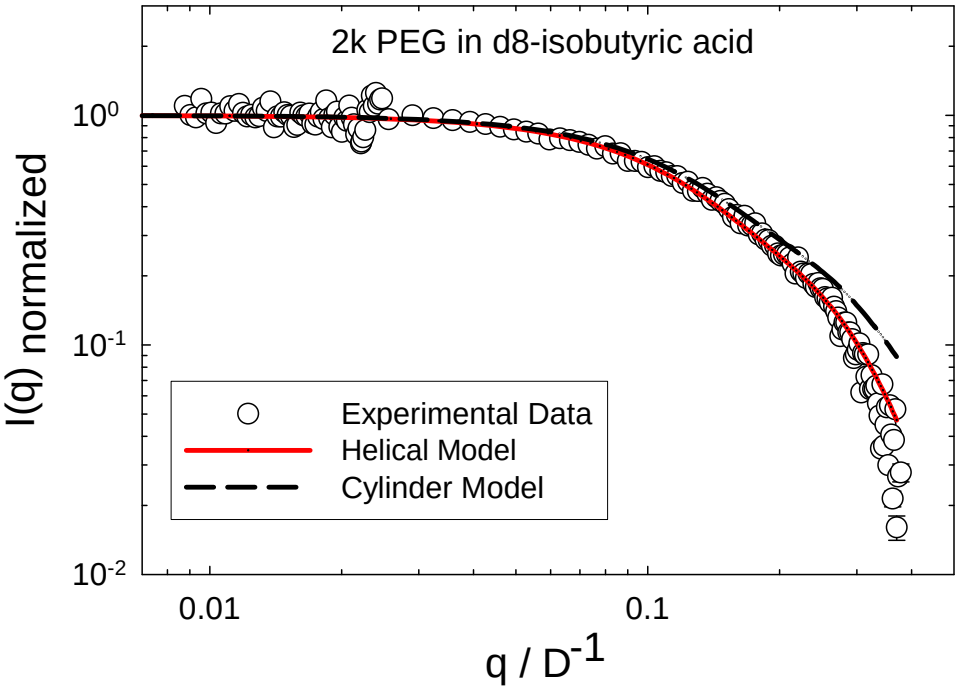
Polymer fractionates and partitions. **WHY? Conformational change?**

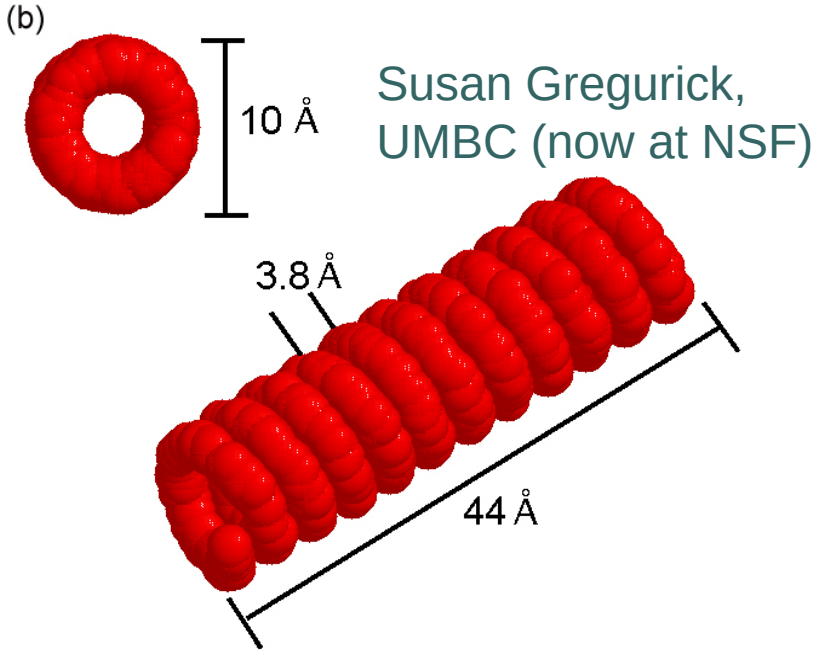
SANS from PEG in d-IBA and D_2O: Very Different …



Sharper interface observed for PEG in d-IBA between particle and solvent

PEG form Helices in d-IBA





Susan Gregurick, UMBC (now at NSF)

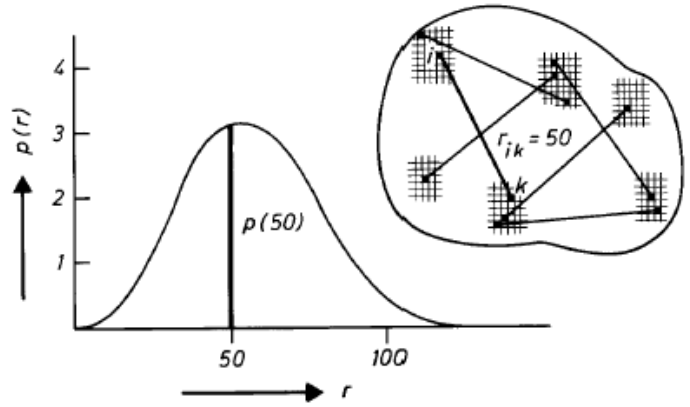
In D_2O chains exist as flexible coils

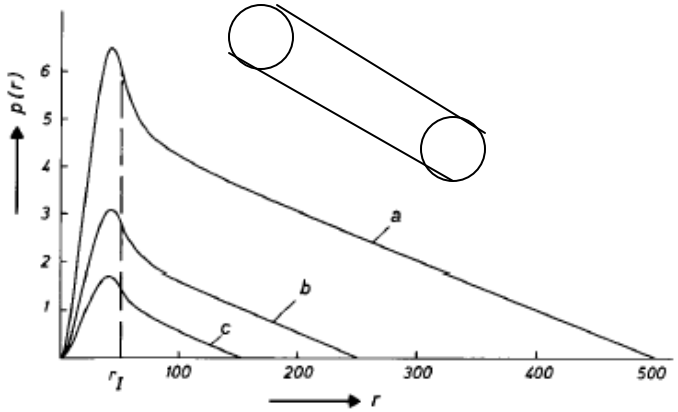
In d-IBA chains exist as tightly wound helices (analogous to coil to globule transition)

Conformational change allows polymers to be separated by MW easily

The PDDF: SANS data in Real Space

The Pair Distance Distribution Function, PDDF or *p(r)* is defined as:



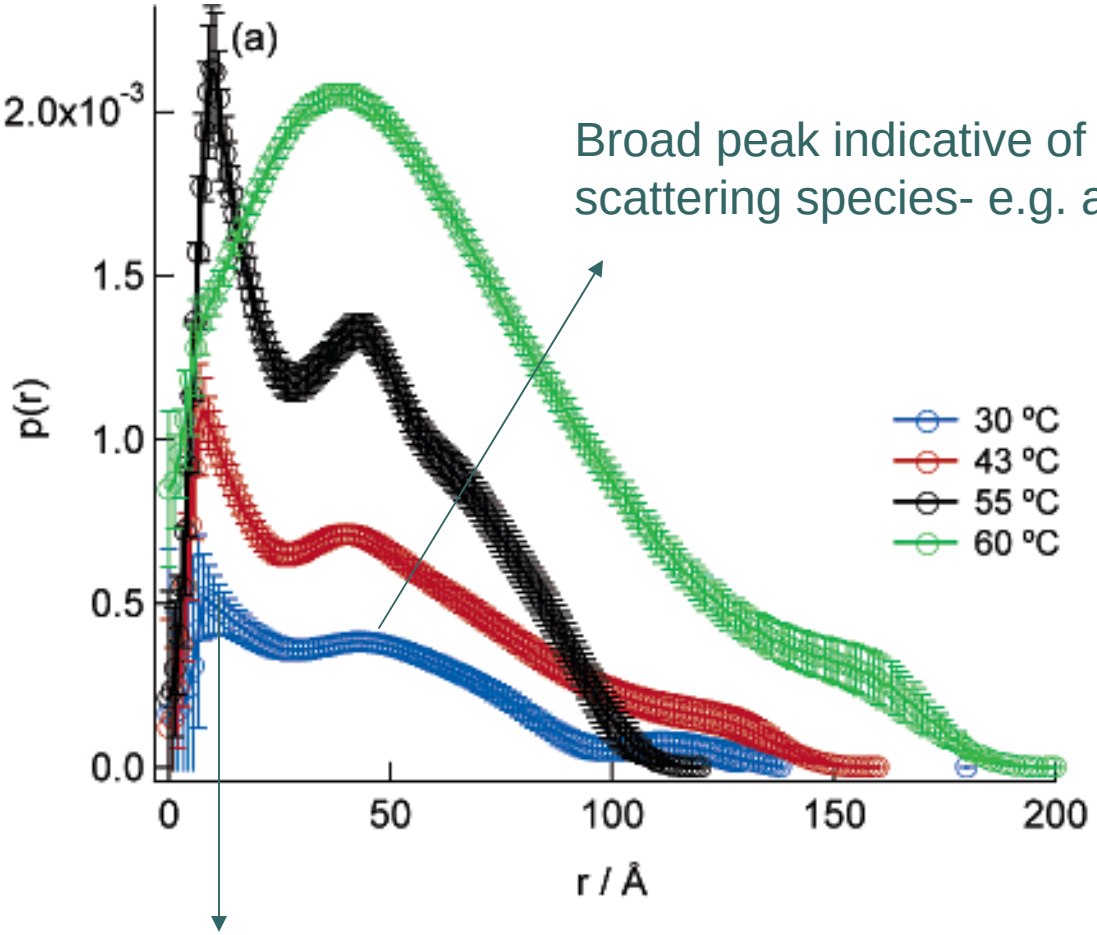


$p(r) \propto$ product of the different scattering lengths of two small volume elements (*i* and *j)* with a centre-to-centre distance between *r*+*dr* and *r*.

All pairs with this distance are summed up together. The height of the *p(r)* function is $\propto$ to the number of distances that can be found inside the particle with the interval *r* and *r* + *dr*.

$$p(r) = \frac{1}{2\pi^2}\int_0^\infty I(q)qr.sin(qr).dq$$

PDDF for PEG in d-IBA and D_2O



Broad peak indicative of spherical-like scattering species- e.g. a coil

Coexistence of rods (helices) and coils at higher molecular weight (20,000 g/mol shown here).

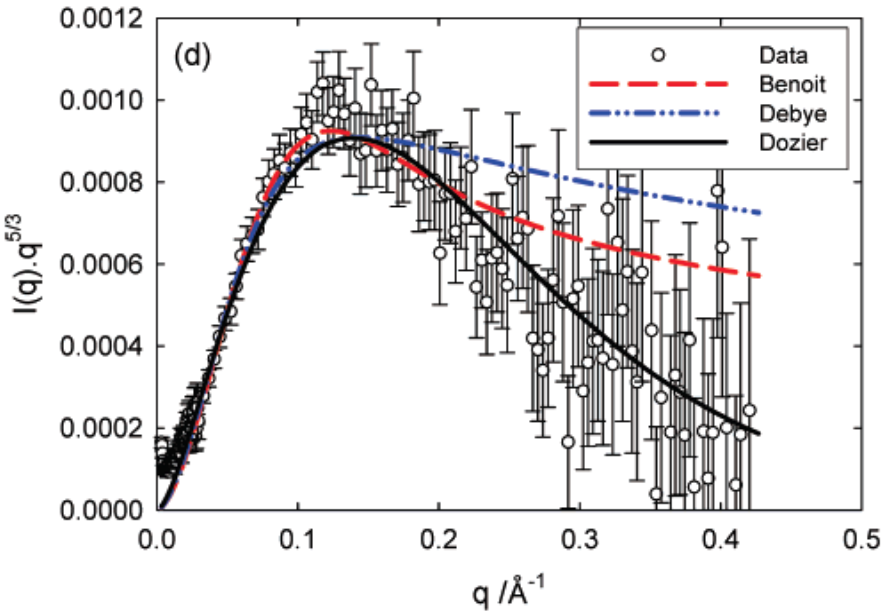
Helices unfold back to coils at elevated temperatures

First sharp peak indicative of rods

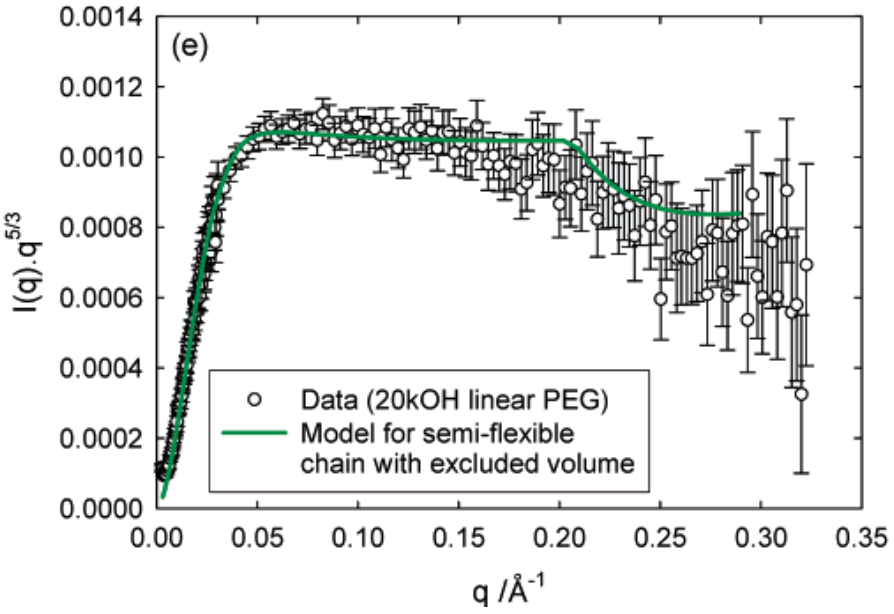
Star Polymers

Star polymers, often thought of as “ultra soft colloids” have industrial relevance for melt-strengtheners and coating applications.

Debye plot: $I(q).q^{1/\upsilon}$,where υ is the Flory exponent (2 for Gaussian chains, 3/5 for chains with excluded volume, i.e polymer coils in good solvent)

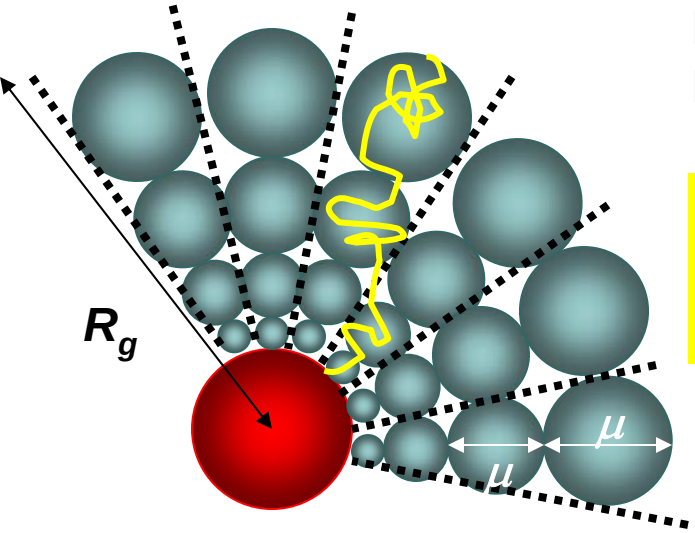


4-arm star PEG: peak in Debye plot



linear PEG: no peak in Debye plot

Star Polymers



Models available for star polymers: Dozier, Huang and Fetters based on **Cotton and Daoud Blob model**

$$I(q) = I(0)\exp\left[\frac{-q^2 R_{g,star}{}^2}{3}\right] + \frac{4\pi\alpha}{q\xi}\left[\frac{\sin\left\{\mu \tan^{-1}(q\xi)\right\}}{(1+q^2\xi^2)^{\mu/2}}\right]\Gamma(\mu)$$

$$R_{g,Star} = R_{g,arm}\left[\frac{3f-2}{f}\right]^{1/2}$$

Polymer modeled as a succession of concentric rings of blobs of size, ξ. Within each blob, the polymer chain is described as a self-avoiding walk with excluded volume, i.e. a coil.

Used for star poly(isoprene), star poly(styrene) and star (polybutadiene) in good solvents.

Model works for star PEG in D_2O but not for star PEG in d-IBA because the arms are helical and not coils.

Concluding Remarks

- SANS is not just beneficial, it is crucial to fully understanding industrial commodity and specialty polymers
  - Structure and Dynamics
  - Conformation
  - Extent of branching
  - What molecules go where- e.g. Shish-Kebab morphology
  - Tie chains
- Ability to selectively deuterate materials or parts of materials gives SANS huge advantages over other scattering methods
- Not only polymer science but studies into proteins, porosity of natural resources such as coal and sandstones possible.
- Developments in instrumentation and software crucial to the continued success of SANS as a tool for industry to use to retain competitive advantage

References and Further Reading

- Tie chain measurements
  - R. L. McCullough, *J. Pol. Sci. Poly. Phys.,* **15**, 1805 (1997)
  - E. W. Fischer, *Polymer J.* **17**, 307 (1985)
- Long chain branching
  - R. Ramachandran, G. Beaucage, A. Kulkarni, D. McFadden, J. Merrick-Mack, V. Galiatsatos, *Macromolecules*, **42**, 4746-4750 (2009)
  - G. Beaucage, *Phys. Rev. E.*, **70**, 10 (2004)
  - G. Beacage, *Biophys. J.* **95**, 503-509 (2008)
- Shish-Kebab morphology
  - S. Kimata, T. Sakurai, Y. Nozue, T. Kasahara, N. Yamaguchi, T. Karino, M. Shibayama, J. A. Kornfield, *Science*, **316**, 1014 (2007)
  - M. Seki, D. W. Thurman, J. P. Oberhauser, J. A. Kornfield, *Macromolecules*, **35**, 2583-2594 (2002)
- Star polymers
  - A. I. Norman, D. L. Ho, S. C. Greer, *Macromolecules,* **40**, 9628-9639 (2007)
  - M. Alessi, A. I. Norman, S. E. Knowlton, D. L. Ho and S. C. Greer, *Macromolecules,* **38**, 9333-9340 (2005)
  - A. I. Norman, Y. Fei, D. L. Ho, S. C. Greer, *Macromolecules,* **40**, 2559-2567 (2007)
  - W. D. Dozier, J. S Huang, L. J. Fetters, *Macromolecules*, **24**, 2810-2814 (1991)
  - M. Daoud, J. P. Cotton, *J. Physique*, **43**, 531-538 (1982)

References and Further Reading

- Books
  - Ryong-Joon Roe, *Methods of X-Ray and Neutron Scattering in Polymer Science,* Oxford University Press, 2000
  - P. Lindner, T. Zemb (Ed), *Neutrons, X-Rays and Light: Scattering Methods Applied to Soft Condensed Matter*, Elsevier, First Ed. 2002