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: SRI Consulting

World Consumption of LLDPE—2008

Source: Phillip Townsend

Market Volume, KT

Source: Nexant/Chem Systems
PERP Report LLDPE 2008

NCNR Summer School May 13, 2010
Polypropylene (PP)

Source: Nexant/Chem Systems
PERP Report LLDPE 2008

World Consumption of Propylene—2008

Source: SRI Consulting

Source: Lawson and Spiller, ExxonMobil Chemical

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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

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

Crystal regions act as anchors for neighboring tie chains.
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$_2$S can form which corrodes metal flow lines. Huge cost disadvantage and lower lifetime of well.

**Use Plastic Pipes:**

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).

**BY CONTROLLING THE COMONOMER DISTRIBUTION WE CONTROL THE TIE CHAINS AND DICTATE MECHANICAL PROPERTIES**
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 into 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, $N_c$. 

$R_g, \text{melt} = R_g, \text{crystal}$
Measurement of Tie Chains

\[
\frac{1}{I(q)} = \frac{1}{N_s} \left[ 1 + \frac{1}{3} q^2 R_g^2 \right] \quad \text{Number of stems per molecule at small } q
\]

\[
\frac{1}{I(q)} = \frac{1}{N_c + 1} \left[ 1 + \frac{N_c}{2(N_c - 1)} q^2 R_g^2 \right] \quad \text{Number of stems per cluster at intermediate } q
\]

\[
\nu = \frac{N_s}{N_c} \quad \text{Number of clusters per molecule}
\]

\[
\nu - 1 \quad \text{Minimum number of tie chains}
\]

\[
P(t) = (\nu - 1) \times \frac{100}{N_c} \quad \text{Probability of tie chains (\%)}
\]
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

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

\[ I(q) = \{ G_2 e^{-(q^2 R_g^2)/3} + B_2 e^{-(q^2 R_{g1}^2)/3} (q_{z}^*)^{-d_{l1}} \} + \{ G_1 e^{-(q^2 R_{g1}^2)/3} + B_1 (q_{1}^*)^{-1} \} \]

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

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

\[ I(q) = B_f q^{-d_f} \text{ for } 1 \leq d_{f} < 3 \]

\[ p = \text{minimum path in Kuhn steps} \]

\[ c = \text{connectivity dimension} \]

\[ z = \text{chain length} \]

\[ d_{min} = \text{average minimum path dimension} \]

\[ B_f, G = \text{scaling prefactors} \]
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**.

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??**

Diagram courtesy of A.J. Bons, private communication
Blown Film Line: Polyethylene
Molecular Origin of Shish-Kebab Morphology

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

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

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

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.
PEG added to a binary mixture of IBA and H$_2$O. Heated above criticality and cooled to 2 phase region. Each phase (upper IBA-rich and lower H$_2$O-rich) assessed for PEG content. Polymer fractionates and partitions. **WHY? Conformational change?**
SANS from PEG in d-IBA and D$_2$O: Very Different ...

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

COIL
Slope = -1.66 (+/- 0.13)

ROD
Slope = -0.987 (+/- 0.007)

D$_2$O at 55ºC
d-IBA at 55 ºC
In D$_2$O 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 Pair Distance Distribution Function, PDDF or $p(r)$ is defined as:

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

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$_2$O

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.

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

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

Debye plot: \( I(q)q^{1/\nu} \), where \( \nu \) 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**

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

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

Polymer modeled as a succession of concentric rings of blobs of size, \(\xi\). 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**

- **Long chain branching**

- **Shish-Kebab morphology**

- **Star polymers**
References and Further Reading

Books