SMALL ANGLE X-RAY AND NEUTRON SCATTERING IN CRYSTALLINE & LIQUID CRYSTALLINE POLYMERS

G. Ungar
Department of Engineering Materials
University of Sheffield, Sheffield, United Kingdom
Email: g.ungar@sheffield.ac.uk

ABSTRACT
SMALL ANGLE X-RAY AND NEUTRON SCATTERING IN CRYSTALLINE & LIQUID CRYSTALLINE POLYMERS.
SAXS has been used extensively in the study of semicrystalline polymers since the earliest days, since the typical dimensions of the lamellar or microfibrillar crystals encountered in such systems are intrinsically on the 10 - 50 nm scale. Although true one-dimensional long range order is not attainable, stacking of lamellar crystals can be highly periodic, so that Bragg diffraction is often used as an approximation to obtain the “long period”. With the advent of synchrotron radiation, with high brilliance and highly collimated beam, SAXS has gain unprecedented power, with numerous time-resolved and high-resolution applications. These will be illustrated on examples of conventional polymers, as well as on model monodisperse oligomers. A further area of application of SAXS is mesomorphic phases in block-copolymers and thermotropic and lyotropic liquid crystals, which includes liquid crystal polymers and dendrimers; some of these applications will be described briefly.

Like SAXS, SANS has found numerous applications in polymer solutions and solid polymers, both amorphous crystalline and liquid crystalline. By isotopic labelling, particularly deuteration, information on the trajectory of a polymer chain in the bulk can be obtained. Following the change in the trajectory occurring upon crystallization, a number of hitherto contentious issues regarding polymer morphology and the crystallization process have been settled. Selective deuteration of parts of the chains, such as chain ends, can result in particularly informative SANS experiments, especially in combination with SAXS data. Carefully chosen labeling can even bring about a high enough contrast to allow real-time SANS monitoring of rapid polymer crystallization, with recording speeds comparable with those of synchrotron SAXS. Examples will be illustrated.

Keywords : SAXS, SANS, synchrotron, crystallization, liquid crystals

SAXS AND SANS IN MODEL CRYSTALLINE POLYMERS

Structural hierarchy in semicrystalline polymers
Atomic scale - crystal unit cell:
- several Angstroms (<1 nm to a few nm)
- detailed crystal structure, conformation of individual bonds
- wide-angle XRD

Scale of crystal thickness:
- 100 - 500 Å (10 - 50 nm)
- electron microscopy, small-angle XRD

Scale of crystal aggregates (spherulites etc.):
- μm scale
- optical microscopy

Figure 1. Polyethylene from 0.1% xylene solution (AFM – atomic force microscopy)
**Structure of lamellar polymer crystals**

- Lamellar crystals thickness 10 nm (typically from solution)
- Polymer chains normal to lamellar surface
- Typical length of extended polymer chain: 1 mm = 1000 nm
- What is the structure?

![Figure 2. Chain-folded lamellar crystal](image)

**What about melt-crystallized polymers?**

- Also lamellar crystals?
- Small-angle X-ray scattering (SAXS) suggests so.
- Diffraction peak at small 2q corresponds to d-spacing 20 – 50 nm = “long period” l
  - stacking of lamellar crystals

**Stacked melt-crystallized lamellae**

![Figure 3. SAXS of oriented i-PP](image)

- Folds less regular
- Amorphous phase more liquid-like
- Stacking often irregular:
  - analysed via 1-d correlation function

**Microfibrillar structure of drawn semi-crystalline polymers**

- crystalline
- amorphous
- microfibril

**Lamellar structure in melt-crystallized PE**

![Figure 4. SEM of surface of PE from which low MW fraction was extracted](image)

**Ultralong Monodisperse n-Alkanes**

- Very long, up to C$_{390}$H$_{782}$
- Strictly uniform in length
- Ideal models for studying fundamental physical properties of crystalline polymers, e.g. polyethylene

<table>
<thead>
<tr>
<th>chain conform.</th>
<th>E</th>
<th>F2</th>
<th>F3</th>
<th>F4</th>
<th>F5</th>
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<td>paraffin</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>C$<em>{150}$H$</em>{302}$</td>
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<tr>
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<td>+</td>
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<tr>
<td>C$<em>{390}$H$</em>{782}$</td>
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<td>+</td>
</tr>
</tbody>
</table>
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Figure 5. AFM micrograph of fracture surface of extended C390. Note chain tilt.

Paths to Integer Folding from Solution

Nature of the Non-Integer Form (NIF)?

Quantized thickening of C_{390}H_{782} lamellae

Subsequent transformation to a mixed integer form
**True nature of NIF and its transformations**

From time-resolved SAXS and SANS:

- Melt
  - low $T_c$
  - high $T_c$

NIF

- E
- F2
- FE

Fast real-time SANS on end-deuterated alkanes to complement real-time SAXS

\[ \text{D}_{25}\text{C}_{12} \cdots \text{C}_{192}\text{H}_{384} \cdots \text{C}_{12}\text{D}_{25} \]

(C216D)

Real-time SANS of isothermal crystallization of C216D at 4 temperatures

(a) 
(b) 
(c) 
(d)
**ED and SLD profiles of the final folded-extended form**

![Graph showing ED and SLD profiles](image)

**SAXS and SANS compared**

![Graph comparing SAXS and SANS profiles](image)

**Binary mixtures of long alkanes**

Model polymer systems with controlled polydispersity.
- C_{16}H_{32} + C_{24}H_{49} 1:1 w:w
- C_{16}H_{32} (208 Å):
- C_{24}H_{49} (315 Å):

Short alkanes (<50 C-atoms) do not co-crystallize.

**SAXS, C_{16}H_{32}+C_{24}H_{49} cooling**

![Graph showing SAXS and SANS profiles](image)

**Selective Deuteration**

C_{16}H_{32}D-C_{24}H_{49} C_{16}H_{32}C_{24}H_{49}D

**Semicrystalline (high T)**

**Superlattice (low T)**

![Graph showing SAXS and SANS profiles](image)
Increasing amorphous layer thickness in semicrystalline form by increasing chain length difference

\[ C_{122} + C_{162} \]

Chain tilt is confirmed.
Accurate detail of “rough” crystalline-amorphous interface.
Gradual dissipation of orientational order of chains emanating from crystal.
SOME APPLICATIONS OF SMALL-ANGLE X-RAY SCATTERING IN COMPLEX LIQUID CRYSTALLINE SYSTEMS

Contents:
1. 3d L.C. phases in molecules with low taper
2. 3d L.C. phases in molecules with high taper (dendrons)
3. 2d columnar honeycombs

Common Liquid Crystal Phases

Electron Density Maps
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Hexagonal p6mm

Rectangular c2mm

Oblique p2

electron density

II-43

Molecular Dynamics Simulation

Polymethylsiloxanes with hemiphasmid side chains

R3m Mesh Phase

Sections through hole - increasing hole diameter

siloxane aromatic aliphatic

- 23 -
**Directly reconstructed electron density of R3m**

- higher
- lower

**Highest electron density regions**
- polysiloxane backbones
  (4 unit cells)

**The three “bicontinuous” (double network) phases in liquid crystals and block copolymers**

- Ia3d bicontinuous cubic (“gyroid”)

<table>
<thead>
<tr>
<th>Ia3d (G)</th>
<th>Pn3m (D)</th>
<th>Im3m (P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>blue:</td>
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<td>blue:</td>
</tr>
<tr>
<td>siloxane (high)</td>
<td>siloxane (high)</td>
<td>siloxane (high)</td>
</tr>
<tr>
<td>yellow:</td>
<td>yellow:</td>
<td>yellow:</td>
</tr>
<tr>
<td>alkyl chain ends (G-surface)</td>
<td>alkyl chain ends (G-surface)</td>
<td>alkyl chain ends (G-surface)</td>
</tr>
</tbody>
</table>

**Im3m - First Triple Network LC Phase**

**BCC phase, dendronized polyoxazoline**

Electron density map

*Nature Materials, 2005, 4, 562*
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**TEM of BCC in Polyoxazoline**

![TEM of BCC in Polyoxazoline](image)


**Alternative Pm3n Structures- different phase combinations**

- **Spheres**

- **Interlocking Columns**

**Location of rubidium**

![Location of rubidium](image)

*JACS*, 2003, 125, 15974

**The two tetrahedrally close packed (TCP) – or Frank-Kasper phases in thermotropic LC**

**Small-angle XRD of a monodomain of the tetragonal P42/mnm phase**

![Small-angle XRD of a monodomain of the tetragonal P42/mnm phase](image)

*Science*, 2003, 299, 1208

tetragonal, $P4_2/mnm$

**Electron Density Maps**

![Electron Density Maps](image)

- $z=0$
- $z=1/4$
- $z=3/4$
- $z=1/2$

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"Isomorphous replacement"

- targeted labeling with electron-rich atoms
Analogues in Transition-Metal Alloys

- BCC α-iron
- Pm3n Cr3Si
- P4_2/mnm Fe-Cr σ-phase

A single atom in alloys A 10^3-10^4-atom micelle

Inverse micelles

Soft spheres: \( d < 2r \)

Inverse micelles and dendrimers: holes are very costly
\( \Rightarrow \) tetrahedral holes cheapest
\( \Rightarrow \) TCP structures

Compromise for hard spheres:
FCC or HCP. Include large octahedral interstices.

Temperature-induced transition

LC Phases in 3,4,5-Trialkoxygallates

Unknown Phase
Found between 2-d columnar and 3-d micellar phases
Dodecagonal Phase: Single Domain X-ray Diffraction

Pattern repeats every $30^\circ$ on rotation around horizontal axis.

12-fold symmetry?

X-ray parallel to axis:
- clear 12-fold symmetry.

→ Dodecagonal liquid quasicrystal.

Penrose tilings

2-D

3-D

Indexing of Single Crystal Diffraction Pattern

Yellow circles – calculated from model


Why do different dendrons form different 3-d phases?

Non-ionic surfactant C12EO12 + water
2-d columnar honeycombs
LC molecules containing 3 types of incompatible blocks

**Triblock Amphiphiles**

- Rigid aromatic unit
- Flexible non-polar chain
- Polar group

**Bolaamphiphile**

**Facial Amphiphile**

*decreasing polar chain length (purple)*

Topological duals on 32434 net

**COWORKERS**

Sheffield
- X.B. Zeng
- Y. Liu
- D.R. Dukeson
- V.S.K. Balagurusamy
- D. Yeardley
- J. Hobbs

Pennsylvania
- V. Percec
- W.D. Cho
- G. Johansson
- N.M. Holec
da
- A. Dulcey

Halle
- C. Tschierske
- S. Diehle
- U. Baumeister
- B. Chen

**CONCLUSIONS**

- Of the three “micellar” 3-d ordered phases (BCC, Pm3n and P42/mnm) two are TCP structures (Frank-Kasper phases).
- First nanoscale quasicrystal. Potential scale-up to self-assembled photonic (wide isotropic PBG) materials.
- Radial volume distribution function – allows prediction of phase structure from molecular architecture
- Pentagonal columnar phase observed. Possibility of columnar liquid quasicrystal.