Quantification of the Macromolecular/Nanoscale Topology using Small Angle Neutron and X-ray Scattering

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LyondellBasell Corporation
(Equistar)
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HFIR
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NIST
Center for Neutron Scattering

Advances in Polyolefins 2009
Hyperbranched Randomly Branched Structures

Long Chain Branching  Short Chain Branching  Hyperbranched

Controlled Branched Structures

Star  Comb  Dendrimer  Cyclic
Randomly Branched Structures

Long Chain Branching


Short Chain Branching


Hyperbranched


Controlled Branched Structures

Star

Comb

Dendrimer

Cyclic

Several Papers in Preparation (2009).
Randomly Branched Structures

Long Chain Branching  Short Chain Branching  Hyperbranched

Nano-scale Aggregates  Biomolecules


The SAXS Experiment

Source  Collimation  Sample  Detector

\[ q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) = \frac{2\pi}{d} \]

\[ I(q) = Nn_e^2 = A^2(q) \]
Fractal Hierarchical Structure
Long Chain Branched Hydrogenated Polybutadiene
(Polyethylene)
Fractal Hierarchical Structure
Long Chain Branched Hydrogenated Polybutadiene
(Polyethylene)

\[ z \sim (R/l_K)^{df} \]

\[ I \sim z \]

\[ q \sim 1/d \sim (l_K/R) \]

\[ I(q) \sim q^{df} \]
Fractal Hierarchical Structure
Long Chain Branched Hydrogenated Polybutadiene
(Polyethylene)

\[ I(q) \sim q^{df} \]
Unified Function Builds Hierarchy Through Structural Levels

Fig. 10. Log-log plot of Debye equation (○) and equation (24) (solid line). For the Debye equation, \( R_g = 50 \, \text{Å} \) and \( A = 100 \, \text{cm}^{-1} \). For the unified equation, (24), all parameters are fixed. \( R_g = 50 \, \text{Å}, G = 100 \, \text{cm}^{-1} \), \( P = 2 \) (the Debye equation represents a mass fractal with \( d_f = 2 \)) and \( B = 0.08 = 2G/R_g^2 \) from equation (30).

Fig. 11. Calculated scattering (○) from polydisperse spheres with Porod surfaces (power law \(-4\)). The solid line follows equation (24) with \( R_g = 39.495 \, \text{Å} \) as calculated and \( P = 4 \), \( G = 100 \, \text{cm}^{-1} \) (fixed in the sphere calculation) and \( B = 0.00012752 \) from Porod’s law.

Porod Regime

Fractal Regime

Unified Function Builds Hierarchy Through Structural Levels

Fig. 12. Calculated scattering curve for an ellipsoid of revolution with a sphenoidal shell of lower electron density, 0.36 of core, with major:minor axis ratio of 4:1 and minor axis of $R = 30 \text{ Å}$ and 60 Å for the core and shell, respectively. Equation (24) is calculated using $R_p = 87.9$, $G = 100 \text{ cm}^{-1}$, $P = 4.91$ and $B = 1.99 \times 10^{-8}$. The mismatch at $q = 0.07 \text{ Å}^{-1}$ is due to a residual Fourier peak that has not been averaged out and that would normally not appear in experimental data for a diffuse interface.

Fig. 13. Calculated scattering curve [Guinier & Fournet, 1955, p. 19, equation (33)] from randomly oriented rods of diameter 40 Å and length 800 Å (+), $L(0)$ is fixed at 100. The calculated scattering curve using equation (28) is shown by the bold line, and $G = 100$, $R_p = 281.4 \text{ Å}$, $P = 1$, $B = 0.393$, $R_{sub} = R_g = 17.3 \text{ Å}$, $G_s = 0.111$, $B_s = 6.25 \times 10^{-3}$ and $P_s = 4$ as discussed in the text. High-$q$ oscillations in the $+\text{ curve are due to poor averaging in the calculation.}^7$

Fig. 14. Calculated scattering curve [Guinier & Fournet, 1955, p. 19, equation (33)] from randomly oriented disc-like lamellae of thickness 40 Å and diameter 800 Å (+), $L(0)$ is fixed at 100. The calculated scattering curve using equation (28) is shown by the bold line, and $G = 100$, $R_p = 283.1 \text{ Å}$, $P = 2$, $B = 1.25 \times 10^{-3}$, $R_{sub} = R_g = 20 \text{ Å}$, $G_s = 2.78 \times 10^{-4}$, $B_s = 1.56 \times 10^{-6}$ and $P_s = 4$ as discussed in the text. High-$q$ oscillations in the $+\text{ curve are due to poor averaging in the calculation.}

Unified Function Builds Hierarchy Through Structural Levels

Fractal Hierarchical Structure

\[ P = d_f \]
Persistence is distinct from chain scaling

Persistence is distinct from chain scaling.

Persistence Length vs. $n_{SCB}$ for Polyethylene from SANS

Persistence Length $l_p$ for Short-Chain Branched Polyethylene

$\begin{align*}
  l_p &= l_p^0 + A \exp\left[-\left(\frac{n_{SCB}}{\tau}\right)\right] \\
  l_p^0 &= 8.9661 \pm 0.0788 \text{ Å}, \quad A = -2.1854 \pm 0.0989, \quad \tau = 3.8949 \pm 0.519 \\
\end{align*}$

Limits: 6.78 Å and 8.97 Å

Fractal Hierarchical Structure

\[ P = d_f \]

\[ I(q) \sim q^{d_f} \]
Mass Fractal dimension, $d_f$

$mass = z \sim \left( \frac{R}{d_p} \right)^{d_f}$

- Random Aggregation (right) $d_f \sim 1.8$
- Randomly Branched Gaussian $d_f \sim 2.3$
- Self-Avoiding Walk $d_f = 5/3$

Problem:
- Disk $d_f = 2$
- Gaussian Walk $d_f = 2$

Nano-titania from Spray Flame

$R/d_p = 10, \alpha \sim 1, z \sim 220$

$d_f = \ln(220)/\ln(10) = 2.3$

FIG. 1. Images of (a) balls folded from an aluminum sheet of thickness $h=0.06$ mm and edge size $L=60$ cm and (b) the cut through this ball. Balankin et al. (Phys. Rev. E 75 051117)
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Nano-titania from Spray Flame

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$d_f = \frac{\ln(220)}{\ln(10)} = 2.3$

A measure of topology is not given by $d_f$.

*Disk and coil are topologically different.*

*Foil and disk are topologically similar.*

FIG. 1. Images of (a) balls folded from an aluminum sheet of thickness $h=0.06$ mm and edge size $L=60$ cm and (b) the cut through this ball. Balakin et al. (*Phys. Rev. E* 75 051117)
Complex Structures Can be Decomposed

\[ z \sim \left( \frac{R}{d} \right)^{d_f} \sim p^c \sim s^{d_{\text{min}}} \]

\[ p \sim \left( \frac{R}{d} \right)^{d_{\text{min}}} \]

\[ s \sim \left( \frac{R}{d} \right)^{c} \]

\[ d_f = d_{\text{min}} c \]

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<td>z</td>
<td>27</td>
<td>1.36</td>
<td>12</td>
<td>1.03</td>
<td>22</td>
<td>1.28</td>
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Tortuosity

Connectivity
Complex Structures Can be Decomposed

Tortuosity

Connectivity

\[ z \sim \left( \frac{R}{d} \right)^{d_f} \sim p^c \sim s^{d_{\text{min}}} \]

\[ p \sim \left( \frac{R}{d} \right)^{d_{\text{min}}} \]

\[ s \sim \left( \frac{R}{d} \right)^c \]

\[ d_f = d_{\text{min}} c \]

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<td>( z )</td>
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<td>( p )</td>
<td>( d_{\text{min}} )</td>
<td>( s )</td>
<td>( c )</td>
<td>( R/d )</td>
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<td>1.36</td>
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<td>22</td>
<td>1.28</td>
<td>11.2</td>
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Complex Structures Can be Decomposed

**Tortuosity**

\[
\phi_{Br} = \frac{z - p}{z} = 1 - z^{1/c-1}
\]

0.56

**Connectivity**

\[
\phi_M = \frac{z - s}{z} = 1 - z^{1/d_{min}-1}
\]

0.19

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<tr>
<td>z</td>
<td>df</td>
<td>p</td>
<td>d_{min}</td>
<td>s</td>
<td>c</td>
<td>R/d</td>
</tr>
<tr>
<td>27</td>
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<td>12</td>
<td>1.03</td>
<td>22</td>
<td>1.28</td>
<td>11.2</td>
</tr>
</tbody>
</table>

Consider a Crumpled Sheet

A 2-d Sheet has $c = 2$

$d_{min}$ depends on the extent of crumpling

$df = 2.3$

$d_{min} = 1.15$

$c = 2$

Balakin et al. (Phys. Rev. E 75 051117 (2007))
Disk

\[ d_f = 2 \]
\[ d_{\text{min}} = 1 \]
\[ c = 2 \]

Extended β-sheet
(misfolded protein)

Random Coil

\[ d_f = 2 \]
\[ d_{\text{min}} = 2 \]
\[ c = 1 \]

Unfolded Gaussian chain
We have resolved a complex structure into a topological network of branch sites and a tortuous path through the structure.

Many other interpretations: Consider a sheet of paper and a crumpled sheet.
Neutron & X-ray Scattering

We can “Build” a Scattering Pattern from Structural Components using Some Simple Scattering Laws

- Dilute Solution of Polymer
- Use Deuterated Solvent to Enhance Contrast (for SANS)
- 40 minutes Measurement using 2 mg of Hydrogeneous Sample

\[ l(\theta) \text{ is related to amount } Nn^2 \]
\[ \theta \text{ is related to size/distances} \]
\[ q = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right) \]
\[ d = \frac{2\pi}{q} \]
Small-Angle Scattering for Mass Fractals of Variable Topology

$d_f = 2$
$c = 2$
$d_{\text{min}} = 1$

$d_f = 2$
$c = 1$
$d_{\text{min}} = 2$

Guinier’s Law

\[ I(q) = G e^{-\frac{q^2 R_g^2}{3}} \]

\( G, R_g \)

Power Law

\[ I(q) = B_f q^{-d_f} \]

\( B_f, d_f \)

Thin Disk

\[ d_{\text{min}} = \frac{B_f R_g^{d_f}}{G_2 \Gamma\left(d_f/2\right)} \]

Gaussian Chain

Measure $d_{\text{min}}$, $d_f$ and know or measure $z$:

\[ c = \frac{d_f}{d_{\text{min}}} \]

\[ p = z^{\frac{1}{c}} \]

\[ s = z^{\frac{1}{d_{\text{min}}}} \]

\[ \phi_{\text{Br}} = \frac{z - p}{z} = 1 - z^{\frac{1}{c} - 1} \]

\[ \phi_M = \frac{z - s}{z} = 1 - z^{\frac{1}{d_{\text{min}}}} \]
Persistence is distinct from chain scaling

Persistence is distinct from chain scaling

Branching has a quantifiable signature.

Branching dimensions are obtained by combining local scattering laws.

\[ R_2 \]

\[ d_{\text{min}} = \frac{B_f R_{g,2}^{d_f}}{G_2 \Gamma \left( \frac{d_f}{2} \right)} \]

Quantification of Branching

\[ c = \frac{d_f}{d_{\text{min}}} \quad p = z^{1/c} \quad s = z^{1/d_{\text{min}}} \]

\[ \phi_{Br} = \frac{z - p}{z} = 1 - z^{1/c - 1} \]

\[ z_{Br} = \frac{z\phi_{Br}}{n_{Br,NMR \text{ or } IR}} \]
$n_{Br}$ from SANS (in Good Solvent)

$$r = n_{s,p} \left( \frac{p}{n_{s,p}} \right)^{3/5}$$

$$r = p^{1/d_{min}}$$

$$n_{s,p} = \left[ p^{(1/d_{min})} - (3/5) \right]^{5/2}$$

$$n_{br,p} = n_{s,p} - 1$$

$$n_{k,s} = \frac{p}{n_{br,p} + 1} = \frac{z}{2n_{br} + 1}$$

$$z_{br} = \frac{z \phi_{br} M_{Kuhn}}{n_{br}}$$

$$n_{br} = \frac{z [(5/2d_{f}) - (3/2c)] + [1 - (1/c)] - 1}{2}$$

Table 1. Characterization of Long-Chain Branching in Dow HDB Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>LCB/10<strong>3C</strong>¹³C NMR</th>
<th>Mₙ (g/mol)</th>
<th>PDI (Mₘ/Mₙ)</th>
<th>β</th>
<th>nₚ</th>
<th>nₚ,p</th>
<th>φₚ</th>
<th>zₚ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDB-1</td>
<td>0.026</td>
<td>39 300</td>
<td>1.98</td>
<td>0.073</td>
<td>0.080 ± 0.004</td>
<td>0.047 ± 0.005</td>
<td>0.10 ± 0.02</td>
<td>12 700 ± 1 500</td>
</tr>
<tr>
<td>HDB-2</td>
<td>0.037</td>
<td>41 500</td>
<td>1.93</td>
<td>0.110</td>
<td>0.115 ± 0.005</td>
<td>0.053 ± 0.005</td>
<td>0.14 ± 0.02</td>
<td>17 400 ± 1 600</td>
</tr>
<tr>
<td>HDB-3</td>
<td>0.042</td>
<td>41 200</td>
<td>1.99</td>
<td>0.124</td>
<td>0.144 ± 0.007</td>
<td>0.065 ± 0.005</td>
<td>0.17 ± 0.02</td>
<td>15 600 ± 1 600</td>
</tr>
<tr>
<td>HDB-4</td>
<td>0.080</td>
<td>39 200</td>
<td>2.14</td>
<td>0.224</td>
<td>0.262 ± 0.007</td>
<td>0.090 ± 0.008</td>
<td>0.28 ± 0.03</td>
<td>18 600 ± 1 700</td>
</tr>
</tbody>
</table>

Table 2. Size and Dimensions of Dow HDB Samples Measured from SANS

<table>
<thead>
<tr>
<th>sample</th>
<th>R (Å)</th>
<th>d (Å)</th>
<th>c</th>
<th>l (Å)</th>
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<tbody>
<tr>
<td>HDB-1</td>
<td>95 ± 6</td>
<td>1.70 ± 0.02</td>
<td>1.03 ± 0.01</td>
<td>6.5 ± 0.5</td>
</tr>
<tr>
<td>HDB-2</td>
<td>103 ± 8</td>
<td>1.71 ± 0.02</td>
<td>1.04 ± 0.02</td>
<td>6.7 ± 0.4</td>
</tr>
<tr>
<td>HDB-3</td>
<td>104 ± 8</td>
<td>1.73 ± 0.02</td>
<td>1.05 ± 0.02</td>
<td>6.6 ± 0.5</td>
</tr>
<tr>
<td>HDB-4</td>
<td>79 ± 4</td>
<td>1.78 ± 0.04</td>
<td>1.08 ± 0.03</td>
<td>6.9 ± 0.5</td>
</tr>
</tbody>
</table>


Comparison of $n_{Br}$ from SANS with $\beta$ from NMR for Weakly Branched HDPE Samples

\[ n_{br} = \frac{z[(5/2d_r)-(3/2c)] + [1-(1/c)] - 1}{2} \]


Number of “inner” segments, $n_i$,
The effect of branch-on-branch structure

The Effect of Branch Length, $z_{br}$, on Viscosity Enhancement for Weakly Branched HDPE Samples

The Effect of Branch Length, $z_{br}$, on Viscosity Enhancement for Weakly Branched HDPE Samples

For model (monodisperse) polymers entanglement effects are observed at:

$2.4 \ M_e = 2.4 \times 1250$

$<z_{Br}>_n,1 = 3000 \ g/mole$

$<z_{Br}>_w t,1 = 9000 \ g/mole$

$PDI_{Br} \sim 3$

$(PDI_{Chain} \sim 2)$


A scaling model for complex topologies was presented.

Decompose structure into topological network & tortuous path.

Small-angle scattering can be used as an effective tool for determination of topology in complex hierarchical macromolecules.

Use this information to construct molecular models & growth pathways.

Method is applicable to a wide range of materials: Polymers, star molecules, cyclics, biomolecules, inorganic chain aggregates.

Potential for broad understanding of complex hierarchical structures.

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