

# BRANCHED OR UNBRANCHED FROM A SCATTERING PERSPECTIVE

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## Abstract

Commercial polyolefins are often produced in grades distinguished by claims of branch content, branch length and even branch-on-branch hierarchies. The description of these complex topologies has often been left to the imagination of catalytic chemists since no clear analytic platform exists to challenge the fairly detailed propositions for branch structure. Rheological characterization coupled with NMR spectroscopy and measures of the hydrodynamic size can give some indication of the richness of branching topologies available in commercial polyolefins but these methods do not fully describe complex polyolefin topologies. In collaboration with LyondellBasell we have recently developed a new approach to understanding branched structure using small-angle scattering of neutrons that can elucidate many complicated topological features such as branch-on-branch structure and new topological descriptions of structure. The technique uses only milligrams of sample and can be carried out in less than one hour at a national user facility.

## Introduction

Synthetic and biopolymers display chain structures that often contain complex topologies ranging from star structures and dendrimers to randomly branched structures and cyclics, Figure 1. Generally, these topologies dominate the physical properties of these materials [1].

Techniques for the quantification of topology can involve observation of the mass of the molecule and the encompassing size as measured by the hydrodynamic radius under a non-draining assumption for instance. This approach can lead to the mass-fractal dimension,  $d_f$ , which is related to the packing density of an object (through a logarithmic relationship). Complex objects, however, are not fully described by their density and the mass fractal dimension is insufficient to describe transport properties or electrical conductivity for example. At the opposite extreme spectroscopic techniques can describe local features of a complex structure such as the number of branch sites or local interaction between chemical species. Again, in the absence of other information, spectroscopic descriptions are incomplete while they give a good measure of the number of structural bridging sites per molecule for instance.

A new application of static neutron scattering for the direct quantification of topology has recently been

developed to quantify the topology of branched structures [2]. For example the mole fraction of a molecule in branches,  $\phi_{Br}$ , can be directly determined using this SANS method. Further, quantitative measures of 1) the convolution or tortuosity of the structure and 2) the connectivity of the branching network can be made [2]. The work is of pivotal interest to many areas of the polymer industry including polyolefins where a picture of branch structure has long been sought to correlate with variation in catalyst, precursor and reaction conditions. This description of topology can further be generalized to describe a much wider range of topologies than long-chain branched polyolefins. In this talk we demonstrate the general usefulness of our topological description of complex structures for long and short chain branched polyethylene. We have already applied this approach to disordered nanomaterials such as chain aggregate structures [3-5], hyperbranched polymers [6], cyclic polymers [5,7] and biomolecules [8].

## Topological Model

A complex molecule can be defined by a mass or number of constituent units,  $z$ . Constituent units are Kuhn units for polymer chains, residue units for a protein or primary particles for an aggregate. For the purpose of a general model we consider a constituent unit to be a sphere. The  $z$  spheres in a complex molecule are constructed into chains that course through 3d space following a path that is described by the end-to-end distance,  $R$ . The path may be tortuous or may be direct depending on the synthesis and equilibration conditions. The shortest paths through the molecule that extend across the molecule have less than or equal to  $z$  constituent units. We call the average of these paths the minimum path,  $p$ . Since this path could be considered separate from the complex molecule, and since it is composed of a linear path of spheres, we can measure the mass fractal dimension of this path,  $d_{min}$ ,

$$p = \alpha \left( \frac{R}{d_p} \right)^{d_{min}} \quad (1)$$

where  $p$  is the number of primary units (Kuhn units) of size  $d_p$  in the minimum path and  $R$  is the end-to-end distance of the minimum path and of the entire complex molecule.  $d_{min}$  is less than or equal to the mass fractal dimension for the complex molecule,  $d_f$ ,

$$z = \alpha \left( \frac{R}{d_p} \right)^{d_f} \quad (2)$$

Since both  $z$  and  $p$  are related to  $(R/d_p)$  we can write,

$$z = p^{d_f/d_{\min}} = p^c \quad (3)$$

where  $c$  is called the connectivity dimension. The model has decomposed the mass fractal dimension into two parts, one reflecting network connectivity,  $c$ , and one reflecting convolution or tortuosity,  $d_{\min}$  and  $p$ .

$$d_f = cd_{\min} \quad (4)$$

In analogy to  $p$  and  $d_{\min}$  in equation (1), we can define a number “ $s$ ” associated with the connectivity dimension  $c$ ,

$$s = \alpha \left( \frac{R}{d_p} \right)^c \quad (5)$$

$s$  reflects the number of spheres that would be needed to connect all network junction and end points in the complex molecule (circles in figure 1) by straight lines.  $s$  is smaller or equal to the total mass  $z$ , just as  $p$  is smaller or equal to  $z$ , Figure 2. In analogy to equation (3) we can write,

$$z = s^{d_f/c} = s^{d_{\min}} \quad (6)$$

in other words, the total structure,  $z$ , is the connectivity path raised to the  $d_{\min}$  dimension.

The mole fraction branching in the molecule,  $\phi_{Br}$ , is given by,

$$\phi_{Br} = \frac{z - p}{z} = 1 - z^{1/c - 1} \quad (7)$$

## Determination of Connectivity and Tortuosity by Small-Angle Neutron Scattering

Scattering under the Rayleigh-Gans approximation (x-ray and neutron scattering) is often reduced to generic local scattering laws such as Guinier's law and power law scattering (e. g. Porod's Law). Guinier's law [9-11] is given by,

$$I(q) = G \exp\left(\frac{-q^2 R_g^2}{3}\right) \quad (8)$$

where  $I(q)$  is the scattered intensity,  $q = 4\pi \sin(\theta/2)/\lambda$ ,  $\theta$  is the scattering angle and  $\lambda$  is the wavelength of radiation,  $R_g^2$  is the mean square radius of gyration and  $G$  is defined as  $N_p n_p^2$  where  $N_p$  is the number of polymer coils in a given volume and  $n_p^2$  is a contrast factor equal to the excess number of electrons for the polymer coil compared to the solvent for x-ray scattering. At higher- $q$  the fractal power law scaling equation [9,10] is appropriate for polymer coils,

$$I(q) = B_f q^{-d_f} \quad (9)$$

where  $B_f$  is the power law prefactor and  $d_f$  is the mass fractal dimension that describes the relationship between coil size and mass. These local scattering laws give an account of local features like size and surface or mass scaling. They cannot independently describe topological features like branching [2].

Consider the class of all 2 dimensional objects in terms of the connectivity/tortuosity model. At one extreme is the Brownian linear path where  $z = p$  and  $c = 1$  so  $d_f = c d_{\min} = d_{\min}$ . At the opposite extreme is a regular object where a linear short-circuit path exists through the structure,  $p = R$ , and  $d_{\min} = 1$  so  $d_f = c d_{\min} = c$ . A disk is the unique 2-d object that displays  $d_{\min} = 1$ . Between these extremes we can consider a wide variety of objects by varying  $d_{\min}$  and  $c$  holding  $cd_{\min}$  to 2, Table 1. Figure 5 shows that for Brownian walk and disk scattering with identical Guinier regimes ( $R_g$  and  $G$ ), the signature of an increase in structural connectivity and reduction in structural tortuosity is a shift in the power law prefactor relative to the Guinier regime creating a knee like feature at about  $0.007 \text{ \AA}^{-1}$  for the lower curve.

The shift in the power-law regime relative to the Guinier regime can be quantified through consideration of Debye's (and Peterlin's) approach to the calculation of the scattering function for a linear Brownian chain [12, 13] as modified by Benoit [14] for arbitrary mass-fractal dimension and considering an integral over all possible minimum paths through the complex molecule [2]. The parameter  $d_{\min}$  can be calculated from scattering using (8) and (9) to account for branched structures [2],

$$d_{\min} = \frac{B_f R_g^{d_f}}{G_2 \Gamma\left(\frac{d_f}{2}\right)} \quad (10)$$

where  $G_2$  is the Guinier prefactor (12) for the coil (or the  $q = 0$  intensity),  $R_{g2}$  is the coil radius of gyration (12),  $d_f$  is the mass fractal dimension (13) and  $B_f$  is the power-law prefactor (13). Having  $d_f$  from the power-law slope at

high- $q$  &  $d_{\min}$  from (14),  $c$  is obtained from  $c = d_f/d_{\min}$  and  $p$  from  $z^{1/c}$ .

We will present recent applications of this topological model to high and low density polyolefins of variable branch structure as well as some model branched polymers.

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Table 1.  $d_{\min}$ ,  $c$  and  $d_f$  for simple objects.

Object	$d_{\min}$	$c$	$d_f$
Rod	1	1	1
Disk	1	2	2
Brownian Chain	2	1	2

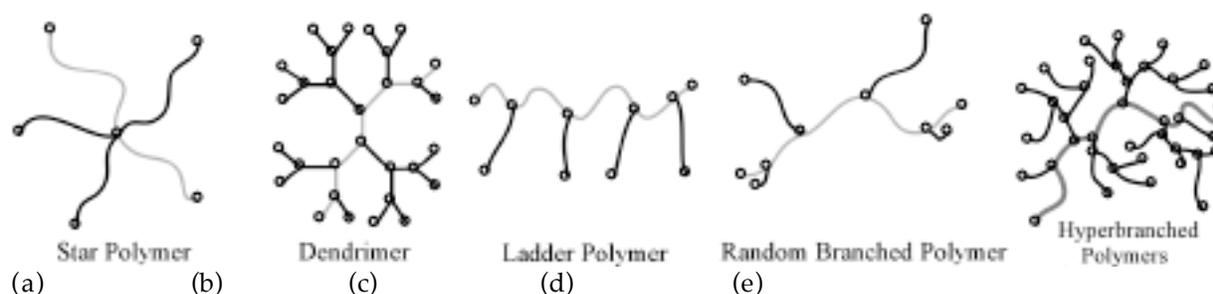


Figure 1. Different branched structures as discussed in text; grey indicates a minimum path of length  $p$  through the molecules; circles indicate points of topological distinguishability (ends or junction points).

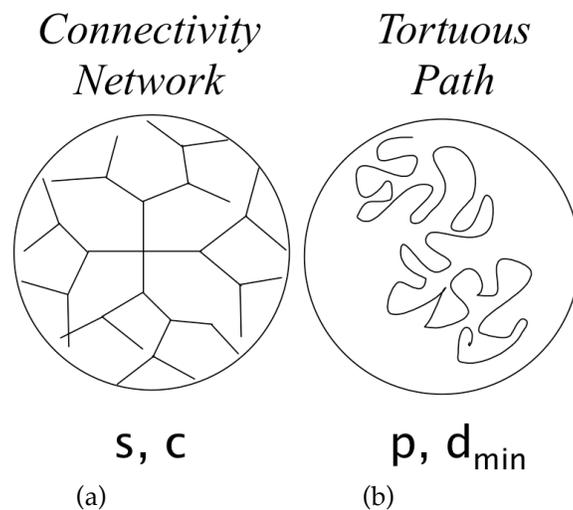


Figure 2. Topological components of a complex molecule. a) network connectivity indicated by straight paths between nodes and free ends of total length  $s$ . b) Structural tortuosity as indicated by minimum path through the structure of length  $p$ .

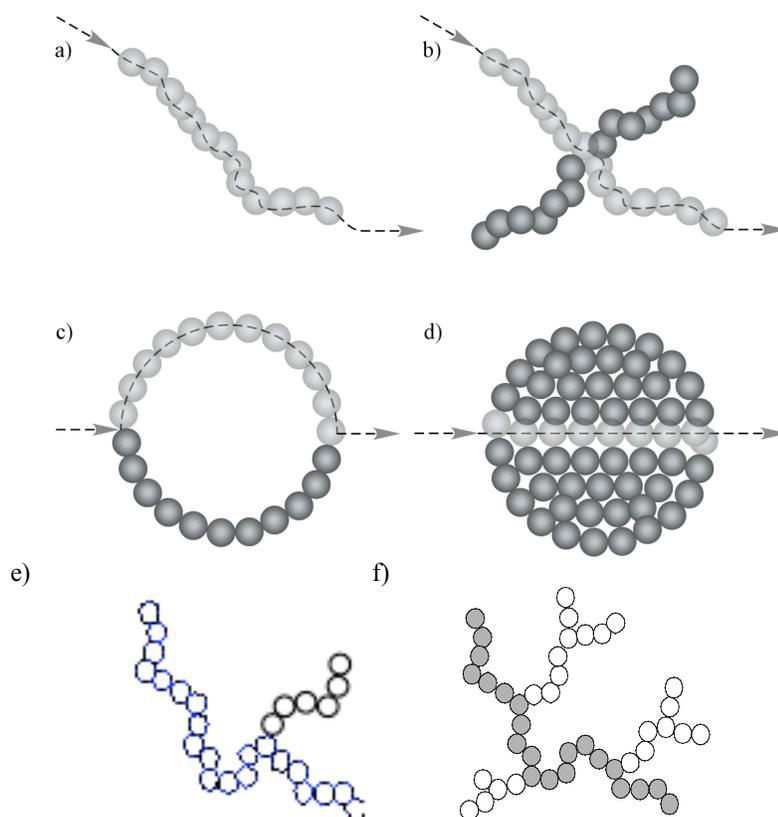


Figure 3. Schematic representation of the minimum path,  $p$ , through a) linear chain, b) 4-arm star, c) cyclic, d) disc, e) a long chain branched aggregate, f) a branch-on-branch structure. The minimum path for a cyclic would constitute half the chain (indicated by the broken line and lighter circles) while the connectivity path,  $s$  would be a straight line across the cyclic.

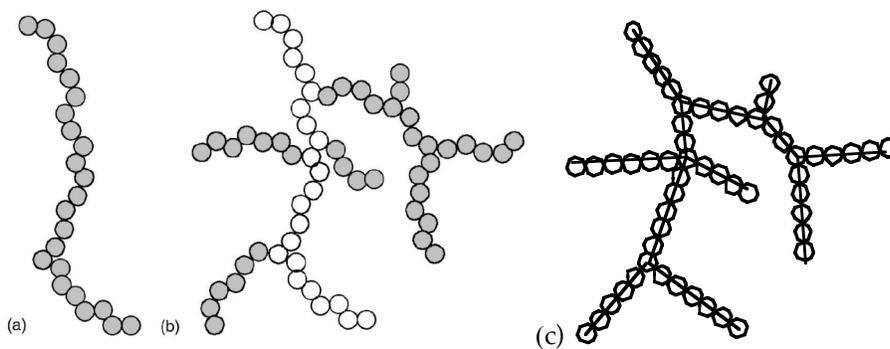


Figure 4. a) Linear aggregate,  $p = 23$ , b) Branched aggregate; composed of primary particles,  $z = 63$ ,  $p = 23$ ,  $s = 54$ ,  $d_f = 1.37$ ,  $c = 1.32$ ,  $d_{min} = 1.04$ . The open circles in b) represent minimum path,  $p$ , through an aggregate [2]. c) deconvoluted structure with  $s$  open circles tracing the path of b) with straight lines,  $s = 54$ .

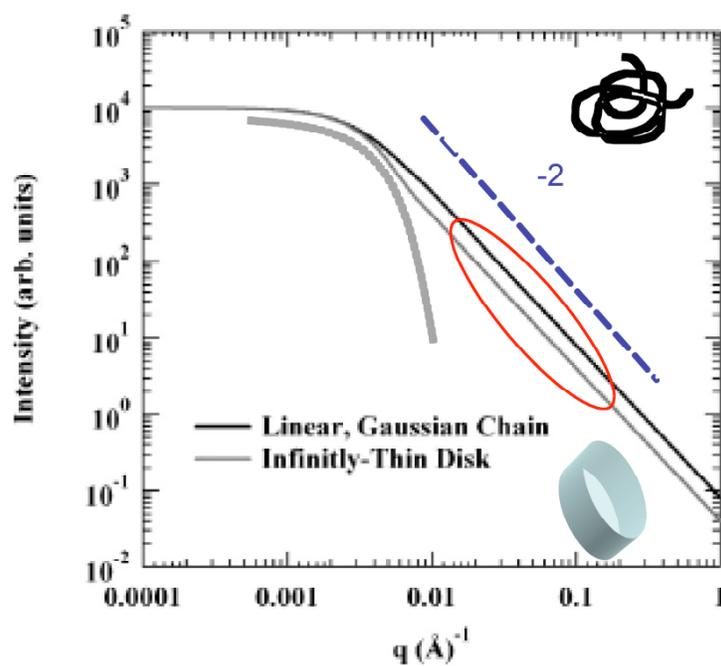


Figure 5. Scattering from a Brownian coil (top and dark) and scaling features for scattering from a thin disk (bottom and grey). Power-law scattering is indicated by the dashed line; Guinier scattering by the exponential decay. Curves are calculated from the unified function. Circled area shows distinguishable feature associated with connectivity/tortuosity of the molecule.