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Quantification of Structural Topology in Branched Polymers

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Quantification of Structural Topology in Branched Polymers

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ABSTRACT

Complex molecular structures occur in various natural and synthetic materials. From common plastics like polyethylene to proteins like hemoglobin, the significant effect of the molecular structure of these materials on their properties cannot be understated. Hence, it is fundamental to comprehensively characterize these complex structures. In the case of polyethylene, branching plays a significant role in determining its structure-property relationships.

Various characterization techniques are available to measure the branch content in polyethylene. Qualitative techniques based on gel permeation chromatography and rheology; and absolute measurements from nuclear magnetic resonance spectroscopy are commonly used to estimate branch content. Drawbacks posed by these common techniques have been well documented in literature. Further, these techniques are unable to provide a comprehensive picture of the structural topology of polyethylene which is crucial to understanding the structure-property relationships of these systems.

In this dissertation, a novel scaling approach is described to quantify branching in polyethylene. The approach is useful in quantifying both short-chain and long-chain branch contents in polyethylene. Additionally, unique measurements such as average long-chain branch length and hyperbranch (branch-on-branch) content are available through this approach. Such enhanced topological information can help us better understand the effect of catalyst systems on
the structure of polyethylene as well as the effect of branching on the polymer’s physical properties.

The scaling approach was successful in quantifying the structure of variety of model and commercial branched polyethylene systems. Specific examples of high-density and linear low-density polyethylene as well as hydrogenated polybutadienes are discussed here. The dissertation is intended to standardize and corroborate the scaling approach in quantifying the structure of branched polymers. The scaling model described in this dissertation is universal. For instance, it can be adapted to quantify the structure of other complex structures such as ceramic aggregates, cyclic polymers and to quantify the degree of folding in protein molecules.
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LIST OF SYMBOLS

Å: Angstrom

$B_f$: Power law pre-factor

c: Connectivity dimension

$C_p$: Polydispersity factor

d$D$: Mass-fractal dimension

d$_{min}$: Minimum path dimension

$\phi_{br}$: Mole-fraction long-chain branch content

G: Guinier pre-factor

$\lambda$: Wavelength

$l_k$: Kuhn’s length

$l_p$: Persistence length

$M_c$: Entanglement molecular weight, g/mol

$M_n$: Number average molar mass, g/mol

$M_w$: Weight average molar mass, g/mol

$M_z$: z-average molar mass, g/mol

$n_{br}$: Average number of branches per chain

$n_{br,p}$: Average number of branches per minimum path

$n_i$: Average number of inner segments per chain

$\eta_0$: Zero shear rate viscosity

p: Minimum path

PDI: Polydispersity Index, $M_w / M_n$

$q$: Scattering vector

$R_g$: Radius of gyration

$\theta$: Scattering angle

$z_{br}$: Average long-chain branch length
CHAPTER I

Introduction
Introduction

I.1 Polyethylene

The phenomenon of branching is widespread in nature. It is seen in simple natural entities like trees, rivers and lightning to complex biological systems such as cells and proteins. Variety of engineering materials such as polymers and ceramic aggregates\(^1\), \(^2\) display structural branching as well. Owing to the influence of branching on the physical and chemical properties, a universal technique is necessary to understand the topology of these materials. For polyolefins like polyethylene, the presence of branching has significant impact on the properties and applications of the polymer.\(^3-6\)

Polyethylene is the most commonly used plastic in the world.\(^7\) It finds uses in a variety of applications from grocery bags and detergent bottles to water pipes and even bullet-proof vests. This is a direct result of the ability to tailor the physical properties of polyethylene to suit various applications. For a commercial polymer with such a variety of applications, polyethylene also has the simplest chemical structure. A linear chain of polyethylene consists of a backbone of even number of carbon atoms that are covalently bonded with a pair of hydrogen atoms attached to each carbon as shown in Figure 1. The chain ends are comprised of methyl groups.
Variations to the structure of polyethylene occur mainly due to presence of branches that affect the properties of these materials. Branching in polyolefins like polyethylene can be classified into short-chain branches (SCB), referring to branches that have only a few carbon atoms and are much smaller than the backbone to which they are attached, and long-chain branches (LCB) where the length of the branch is comparable to that of the backbone. A semi-crystalline polymer like polyethylene has both crystalline and non-crystalline regions. The presence of branches affects the ability of the chains to crystallize and hence affects the overall density of the material. Higher concentration of branching in polyethylene results in lower density of the polymer. Commercially, various grades of polyethylene are classified based on their overall density. The most important classes of polyethylene are described here.
a. High-Density Polyethylene (HDPE)

Among commercially produced polyethylene, high-density polyethylene is structurally closest to linear polyethylene. It primarily consists of unbranched chains that result in relatively higher densities ranging from 0.94-0.97 g/cm$^3$. While HDPE is essentially considered as a linear polymer, this polymer may contain low levels of long-chain branching. Many grades of HDPE are produced by employing various catalysts such as Ziegler-Natta catalysts, metallocene catalysts and chromium oxide catalysts.

b. Low-Density Polyethylene (LDPE)

Low-density polyethylene consists of highly branched polymer chains that result in relatively lower densities ranging from 0.90-0.94 g/cm$^3$. The branches consist of both short-chain and long-chain branches. Hyperbranched (branch-on-branch) structures are typical to this class of polyethylene. LDPE was the first commercial polyethylene to be produced in the industry. Typically, the production of LDPE involves high pressure free radical polymerization process. Due to the nature of this production process, LDPE has a high concentration of branches.

c. Linear Low-Density Polyethylene (LLDPE)

Linear low-density polyethylene is a class of polyethylene that are typically linear with respect to long-chain branches but contain various levels of short-chain branches.
They are named as such since chemically they fall between HDPE and LDPE. The density of LLDPE ranges from 0.90-0.94 g/cm$^3$.\textsuperscript{7} The short-chain branches arise during production because ethylene is copolymerized with $\alpha$-olefins such as butene, hexene and octane using either Ziegler-Natta or metallocene catalysts.\textsuperscript{7-9}

I.2 Quantification of Branching

Apart from the molecular weight of the polyethylene, the molecular structure of polyethylene has significant impact on its physical properties. Structural branching plays an integral role in defining the structure of a polymer. Branching affects a wide array of physical properties such as density, crystallinity, rigidity, hardness, melt strength, permeability, processability and optical properties.\textsuperscript{3-6} For decades, considerable research has been conducted in order to develop analytical method that can provide a comprehensive characterization of the structure of branched polymers.\textsuperscript{10-13} The common techniques that are currently employed along with their drawbacks are described in the ensuing discussion.

a. Nuclear Magnetic Resonance (NMR) spectroscopy

High resolution Carbon-13 Nuclear Magnetic Resonance ($^{13}$C-NMR) spectroscopy is commonly used as a primary technique to quantify branching in terms of the number of branches per 10,000 Carbon atoms or per chain.\textsuperscript{10, 14-16} This technique measures the shifts in the frequency of up to 5 carbon atoms that are attached to a branched carbon which can then be used to estimate the number of branches.\textsuperscript{10, 14} Due to the limitations of the NMR
In other words, while this is a very useful technique in characterizing the number density and type of short-chain branches, it fails to provide an accurate measurement of long-chain branches both in terms of the number density and branch length. NMR can be only be used to effectively quantify branching in polyethylene and polyvinyl chloride.\(^ {10, 14}\) Moreover, the use of the technique involves finding the right balance between desired accuracy and analysis run times.\(^ {12}\)

b. Size Exclusion Chromatography (SEC)

Size exclusion chromatography (or gel permeation chromatography, GPC) is a commonly used secondary technique to quantify branching in polyethylene.\(^ {9, 10, 15, 17}\) SEC separates polymer molecules based on their hydrodynamic size (which is affected by the presence of branches). A variety of detectors can be employed in the downstream end of the SEC such as inline viscometer (VD), refractive index detector (RID), multi-angle laser light scattering (MALLS) that measure the intrinsic viscosity ([\(\eta\)]) and radius of gyration (\(R_g\)) of the fractions separated by SEC. By comparing these measurements with that of a linear polyethylene standard, it is possible to provide estimates for the average number of long-chain branches. Apart from the need for suitable linear standards, the technique faces many drawbacks. Since SEC separates polymer chains based on their hydrodynamic size and not molecular weight, it cannot distinguish, for instance, a branched polyethylene chain and a linear chain of the same size.\(^ {10}\) The accuracy of the
measurements are dependent on the sensitivity of the detectors which are typically not very sensitive to low levels of long-chain branching. Moreover SEC measurements are carried out in good-solvent conditions, whereas the empirical methods that are used to estimate the branch content from SEC are based on theta solvent conditions.

c. Melt Rheological Methods

The presence of long-chain branching in polyethylene has significant impact on the melt rheological properties of polyethylene. It has been previously reported that significant rheological effects are only observed when the branch length is about 2.4 times the entanglement molecular weight, $M_e$, of 1250 g/mole. A variety of semi-empirical quantities such as the Dow Rheology Index (DRI) and Long-chain Branch Index (LCBI) have been proposed that uses rheological data to estimate levels of long-chain branching in polyethylene. DRI cannot distinguish between the effects of polydispersity and branching and hence can only be applied to polymers that have a low polydispersity index ($M_w/M_n<2$). LCBI was developed to overcome the problems associated with DRI. An underlying assumption in this approach involved considering polymers with very low levels of long-chain branching to be linear. But even low levels of long-chain branching can impact the properties of polyethylene. Both DRI and LCBI being semi-empirical in nature are unable to provide reliable and routine quantification of long-chain branches in polyethylene.
Apart from the drawbacks that were mentioned in the previous section, all these common
techniques (NMR, SEC and rheological methods) quantify branching in terms of the number of
long-chain branches. While this is a useful quantity, it alone is not sufficient to describe the
many changes in properties that occur due to the presence of branching. For instance, the
rheological properties of polyethylenes are greatly affected by the length of long-chain branches\(^5\) and the presence of hyperbranched (branch-on-branch) segments.\(^{23}\) A universal scaling model\(^{24}\) has been developed in the past decade to quantify branch content in such ramified structures. The
scaling model has been employed successfully to study ceramic aggregates\(^{24}\) and to describe the
folded and unfolded state in proteins and RNA.\(^{25}\) In this dissertation, this scaling model is
developed and applied to quantify the branch content (both short-chain and long-chain
branching) in model and commercial polyethylene. This model can also be applied to further the
topological understanding of other polymer systems as well as non-polymeric complex
structures. A brief description of the scaling model is given in the following section. More
detailed descriptions are included in the upcoming chapters where the scaling approach is
applied to quantify branching in polyethylene.

I.3 Scaling Model

Polymers like polyethylene (PE) in dilute solution display two structural levels: the
average chain size \(R\) with mass-fractal dimension \(d_f\) and an average substructural rod-like
persistence unit of length, \(l_p\), or Kuhn length, \(l_k \approx 2l_p.\)\(^{26}\) These structural levels are observed in
small-angle scattering patterns from polyethylene. The Unified Function\(^{23, 27-31}\) used in this
dissertation is useful in quantifying these structural levels in terms of their size and associated
mass-fractal dimensions. A branched polymer like polyethylene can be described in terms of two distinct features. One is an average short circuit path (or minimum path) through the branched structure that exhibits an average tortuosity linked to the thermodynamic conditions and steric constraints. The other is an average connectivity based on the branch content, which is not affected by changes in thermodynamic conditions. These two average features of branched polymers can be described using a universal scaling model.\textsuperscript{30} The scaling model has been used previously in describing the structure and quantifying the topology of a variety of mass-fractals.\textsuperscript{10, 23, 25, 29, 30, 32, 33}

Considering a polyethylene chain of end-to-end distance $R$ and mass-fractal dimension $d_f$ composed of $z$ Kuhn steps of size $l_k$ each (see Figure 2), the scaling model describes an average short-circuit path or minimum path $p$ with mass-fractal dimension $d_{\text{min}}$. The tortuosity in the polyethylene chain is described by $p$ and $d_{\text{min}}$. The connectivity of the polyethylene chain can be described by a connecting path $s$ with an associated connectivity dimension, $c$, that is obtained by joining chain ends and branch points with straight lines. $z$, $p$ and $s$ can be related to the chain size $R/l_k$ by,

$$z = \left( \frac{R}{l_k} \right)^{d_f}, \quad p = \left( \frac{R}{l_k} \right)^{d_{\text{min}}} \quad \text{and} \quad s = \left( \frac{R}{l_k} \right)^c$$

(1)

A scaling relationship between $z$, $p$ and $s$ can then be derived as,\textsuperscript{23, 30}

$$z = p^c = s^{d_{\text{min}}}$$

(2)
From Eqs. 1 and 2 a simple relationship is obtained, \( d_f = c d_{\text{min}} \), that shows how chain scaling is described via contributions from tortuosity and connectivity. For regular objects like rods and spheres that are completely connected and have no tortuosity through the structure, \( d_f = c \) and \( d_{\text{min}} = 1 \). \( d_{\text{min}} \) increases with tortuosity, \( c \) increases with increased connectivity (or increased branching). Thus for linear polyethylene in a good solvent, \( d_f = d_{\text{min}} \approx 5/3 \) and \( c = 1 \). For branched polyethylene in a good solvent, \( d_f > d_{\text{min}} \), \( 1 < c \leq d_f \) and \( 1 \leq d_{\text{min}} \leq 5/3 \).

In the scaling approach,\textsuperscript{10, 23, 30, 31} to describe a branched polymer chain of molecular weight \( z \), we define a minimum path, \( p \), which is the molecular weight of the average short-circuit path taken through the polymer chain. The part of the molecule outside of the minimum path, \( z-p \), is then considered to be as branches. Thereby, the mole fraction long-chain branch content, \( \phi_{br} \), is obtained by,

\[
\phi_{br} = \frac{z-p}{z} = 1 - \frac{1}{z^c} \tag{3}
\]
Figure 2. Schematic of a branched polymer in the scaling model. Each Kuhn step is represented by a bead. The polymer of mass-fractal dimension $d_f$ is composed of $z$ Kuhn steps of size $l_k$ each. The dark beads represent the minimum path $p$ of dimension $d_{min}$. The lighter Kuhn steps symbolize the long-chain branches. The dotted lines represent the connective path of size $s$ and dimension $c$. The chains are depicted in a non-overlapping extended conformation in order to distinguish the arms.
The Unified Function\textsuperscript{23, 27-29} along with the scaling model\textsuperscript{30} when applied to small-angle neutron scattering data, from dilute solutions of polyethylene in a good solvent, provides substantial information to quantify the topology of branched polyethylene. For example, the Unified Function in Eq. 4 gives $R_g^2$, $G_2$, $B_2$, $G_1$, $B_1$ and $d_f$.

$$I(q) = \left\{ \begin{array}{l} G_2 e^{-q^2 R_g^2/3} + B_2 e^{-q^2 R_g^2/3} \left( q^2 \right)^{-d_f} + G_1 e^{-q^2 R_g^2/3} + B_1 \left( q^2 \right)^{-1} \end{array} \right\}$$  \hspace{1cm} (4)

$$q^2 = \left[ \frac{q}{\text{erf} (q R_g / \sqrt{6})} \right]$$

where $k \approx 1.06$

The terms in the first bracket with subscript “2” represent the overall chain size and the second bracket with subscript “1” represent the rod-like persistent scaling regime. The minimum dimension, $d_{min}$, is calculated from these parameters and is given by,\textsuperscript{23, 30}

$$d_{min} = \frac{B_2 R_g^2}{C_p \Gamma \left( \frac{d_f}{2} \right) G_2}$$  \hspace{1cm} (5)

where $C_p$ is the polydispersity factor\textsuperscript{23, 29, 34} and $\Gamma$ is the gamma function. The weight-average number of Kuhn steps, $z$, is given by the ratio of $G_2$ over $G_1$.\textsuperscript{28-30} The connectivity dimension, $c$, is obtained from $d_f/d_{min}$ as described in the scaling model. From the topological parameters obtained, an expression is derived\textsuperscript{23} for the weight-average number of branch sites per chain, $n_{br}$, which is given by,\textsuperscript{23}

$$n_{br} = \left( \frac{z \left( \Gamma_{2d_f} - \Gamma_{2c} \right) \left( 1 - \frac{1}{2} \right)}{2} \right)$$  \hspace{1cm} (6)
The weight-average number of branches per chain, $n_{br}$, is comparable to the number of long-chain branches per chain that is obtained from NMR$^{13,23}$ for tri-functional branch points except that the NMR measurement is a number-average. The weight-average long-chain branch length, $z_{br}$, is determined by,

$$z_{br} = \frac{z_{br} M_{Kuhn} \phi_{br}}{n_{br,p}}$$  \hspace{1cm} (7)

where $M_{Kuhn}$ is the mass of one Kuhn step and assuming $f = 3$ (branch site functionality). For polyethylene, $M_{Kuhn} = 13.4 \: l_k$, where $M_{Kuhn}$ has units of g/mole and $l_k$ has units of Å.$^{23}$ $n_{br,p}$ represents the average number of branches per minimum path. Using $n_{br}$ and $n_{br,p}$, an expression for the hyperbranch content in terms of the average number of inner segments per chain, $n_i = n_{br} - n_{br,p}$ is obtained.$^{23}$ Inner segments refer to segments in a polymer that have branch points at both ends.

I.4 Small-Angle Neutron Scattering

Small-angle scattering techniques (light, neutron and X-ray) are frequently used to investigate the structure of materials like polymers. Apart from being non-invasive, these techniques provide structural information that is averaged over the whole sample. In the case of small-angle neutron scattering (SANS), neutrons are scattered by their interactions that with the nuclei of the sample. Analogous to the electron density difference that is utilized for contrast in small-angle X-ray scattering (SAXS) experiments, SANS utilizes the difference in scattering length between the nuclei species in a sample. In the case of hydrogenous systems like
polyethylene, the pronounced difference in scattering length between hydrogen and deuterium is utilized to vary the contrast. In SANS measurements from solutions of hydrogenous polymers, a deuterated solvent is employed to get the desired contrast between the polymer and the solvent. Alternatively, it is possible to deuterate some of the chains in a polymer by replacing the hydrogen atoms with deuterium atoms.

I.4.1 SANS from Polyethylene

The size and dimensions that describe a polyethylene chain in the scaling model are determined from small-angle neutron scattering data that is obtained from very dilute solutions of polyethylene in a deuterated good solvent.\textsuperscript{23, 29, 31} The very dilute solutions with concentrations below the overlap concentration\textsuperscript{35} ensure that quantities measured are representative of an average isolated chain. SANS experiments require neutron sources that are available in the form of steady-state nuclear reactors and spallation sources. Steady-state sources produce neutrons continuously via the nuclear fission process. On the other hand, spallation sources provide a pulsed neutron beam.

In the SANS experiments performed for the current work, a monochromatic cold neutron beam ($\lambda \approx 5\text{Å}$) illuminates the sample (dilute solutions of PE in deuterated good solvent). The scattered neutrons are detected by 2-dimensional position-sensitive detectors. Neutron-absorbing gas molecule like $^3$He is used to convert neutrons (uncharged particles) to charged particles that can be electronically detected. The instrument is evacuated to avoid scattering or absorption by
air. The scattered intensity of neutrons from the sample is measured as a function of the momentum transfer vector (also referred to as the scattering vector), \( q \), which is inversely related to size-scale of the system and described by,

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

(8)

where \( \theta \) is the scattering angle and \( \lambda \) is the wavelength of incident neutrons. A wide \( q \)-range is covered by adjusting the sample-to-detector distance (SDD) from 0.75 m to 18 m. The low SDD corresponds to high-\( q \) and high SDD corresponds to low-\( q \) range. A schematic of the SANS experiment is shown in figure 3.
Figure 3. Top: Schematic of a SANS experiment. Bottom: A panoramic view of the NG7 SANS instrument in NIST. The red cylinder is the evacuated chamber where the detector moves.
SANS was conducted on dilute solutions of polyethylene in deuterated p-xylene which is a good solvent for polyethylene at 125 °C. 1 wt. % solution was used in each experimental run to ensure dilute conditions. The dilute condition is determined by a concentration which is below the overlap concentration. The overlap concentration was determined from the molecular weight of the polymer by the method described by Murase et al. To ascertain that 1 wt. % was below overlap concentration, three different concentrations were examined: 0.25 wt. %, 0.5 wt. % and 1 wt. % for the highest molecular weight polymer sample. The data obtained corrected for concentration differences was superimposable demonstrating concentration below overlap. Standard 2mm path length quartz banjo cells and demountable aluminum cells with quartz windows were used. The polyethylene solutions were prepared by measuring a weighed quantity of the sample into the cell and transferring the deuterated solvent into the cell. 500 ppm of butylhydroxytoluene (BHT) was used as a stabilizer and dissolved in the solvent during sample preparation. BHT was dissolved in the stock solvent before transfer to cell. The samples were equilibrated at 125 °C for 2 to 3 hours prior to the measurements to ensure complete dissolution of polyethylene. Additionally, the polymer solution was stirred by means of micro-magnetic stir bars to ensure proper mixing. The lack of evidence of any Porod scattering at low-\( q \) and repeatability of the measurements after 6 hours at temperature confirms dissolution. The SANS experiments were performed at 125 °C to maintain the solvated state.

SANS experiments were conducted at NG-7 SANS in the National Institute of Standards and Technology (NIST), Gaithersburg and CG2 SANS in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL) and the Intense Pulse Neutron Source (IPNS, now
decommissioned) at Argonne National Laboratory. A sample cell holder equipped with
temperature regulation available at the beam line was utilized. Standard data correction
procedures for background and incoherent scattering along with secondary standards were used
to obtain $I(q)$ vs. $q$ in absolute units. Experimental runs took approximately 2 hours per sample.

Corrected SANS data from dilute solution of polyethylene resin is typically plotted in a
log-log plot of $I(q)$ vs. $q$ as shown in figure 4. Polymers like polyethylene (PE) in dilute solution
display two structural levels: the average chain size $R$ with mass-fractal dimension $d_f$ and an
average substructural rod-like persistence unit of length $l_p^*$ or Kuhn length $h_k \approx 2l_p$.\footnote{Additionally, a dynamic size close to $l_p$ called the packing length [3] can be defined which is not discussed here.} At low and
medium $q$ range, information about the overall size and scaling of the chain is obtained. At high-$q$,
information about the persistence units, that form the building blocks of the PE chains, are
obtained. A solution of linear polyethylene in a good solvent displays good solvent scaling of $d_f$
= 5/3 which is observed as a power law decay in the medium $q$-range of the $I(q)$ vs. $q$ plot. The
persistence units display rod-like scaling of $d_f= 1$ which is observed in the high $q$ range as shown
in figure 4. A long-chain branched polyethylene chain of the same molecular weight will display
a higher mass-fractal dimension, $d_f$, and lower average chain size, $R$, due to its higher density.
These changes to the features are observed in a SANS scattering profile as shown in figure 5.
Standard scattering laws like Guinier’s law and power law are used to extract the sizes and
dimensions of the polyethylene chain.\cite{10, 23, 25, 27-31, 33, 37, 38} Detailed analysis to record such
changes are described in chapters III, IV and V. The persistence length is a measure of the local
structure and is unaffected by the presence of long-chain branches. On the other hand, the
presence of short-chain branches affects the local structure which is measured by an increase in the persistence length of the polyethylene. Chapter II describes in detail the effects of short-chain branching on the persistence length of polyethylene.

**Figure 4.** A typical SANS profile obtained from dilute solution of polyethylene in a good solvent. A linear polyethylene shows the good solvent scaling of 5/3 at low $q$ and rod-like persistence scaling at high $q$. 
Figure 5. SANS profile from a long-chain branched polyethylene chain of the same molecular weight as the linear polyethylene in figure 4.
I.5 Scope of Current Work

While the scaling method\textsuperscript{30} can be adapted to quantify the structure of a variety of complex materials\textsuperscript{25, 30, 33}, this dissertation work focuses on adapting and developing the scaling approach to provide comprehensive quantification of branch content in polymers.\textsuperscript{23, 29, 31} The application of the scaling approach for polymers is standardized and substantiated with polyethylene. Apart from being one of the most important commercial polymers, polyethylene allows the methods described here to be tested for a wide array of structures with different branch types, branch density and polydispersity index. Further, the new quantities that are described and measured in this dissertation are useful in better understanding the effects of processing and catalyst systems on the structure of polyethylene. Essentially, by finding a suitable good solvent, the scaling/SANS method can be applied to quantify the structure of other polymer systems.

The highlights of the topics that are covered in this dissertation are given below:

Chapter II:

The scaling/SANS approach can be used to estimate the persistence length, $l_p$, of polyethylene. $l_p$ is a measure of the local structure of polyethylene which is affected by the presence of short-chain branches. In this chapter, a relationship is determined between the persistence length and short-chain branch content of polyethylene.\textsuperscript{29} Commercial linear low-density polyethylene (LLDPE) with different amount of ethyl short-chain branches were utilized
for this study. The results presented in this chapter are specific to ethyl short-chain branches and the effect of short-chain branch length is discussed further in Chapter V.

Chapter III:

The scaling/SANS approach is applied to a series of model commercial high-density polyethylene resins called the Dow HDB Series.\textsuperscript{23} Not only are these polymers as close to model systems as there are available in commercial polyethylenes, they have also been extensively characterized in literature. The effect of long-chain branching and hyperbranching on rheological properties like zero-shear rate viscosity enhancement is described.

Chapter IV:

The SANS/scaling approach is used to quantify the structure of model 3-arm star hydrogenated polybutadiene resins. These resins serve as ideal analogs polyethylene resins. The results presented in this chapter substantiate the scaling approach as well as confirm that the quantities measured in the approach are weight-averaged quantities. Additionally, some new insights into the effect of anionic polymerization on the structure of polyethylene is described.

Chapter V:

In this chapter, the branch length distribution is studied in a commercial linear low-density polyethylene resin.\textsuperscript{31} By fractionating the polyethylene using temperature rising elution fractionation (TREF), the scaling approach is used to determine how short-chain and long-chain branches are distributed amongst the fractions of a commercial polydisperse resin. The study
provides enhanced understanding of the effect of processing and catalyst systems on the structure of polyethylene.

Chapter VI:

The conclusions of this dissertation are summarized. Additionally, some descriptions of future work resulting from this dissertation are provided.

Appendix A1:

The effect of polydispersity in polyethylene is a major challenge in quantifying branch content using rheological techniques. This is because the effects of long-chain branching and the effects of polydispersity on rheological properties are similar. In the scaling/SANS approach the effect of polydispersity is observed in the low q range of the SANS data. In order to accommodate for polydispersity, a factor called the polydispersity factor, \( C_p \), is introduced in the SANS data analysis using the Unified Function.\(^{23,27-29}\) \( C_p \) is essentially a high order moment of the ratio of molecular weights of polyethylene that can be related to the ratio of \( M_z \) over \( M_w \). In this appendix, the relationship between \( C_p \) and \( M_z/M_w \) is presented for a wide array of polyethylene resins. The results are utilized to standardize the fitting procedure of the SANS data using the Unified Function.

Appendix A2:

As an extension of the results obtained in Chapter III, the effect of hyperbranched segments (branch-on-branch) on the zero-shear rate viscosity enhancement in expanded to other polyethylene systems with higher amounts of long-chain branching. While the behavior observed
is well known, for the first time, it is possible to relate the viscosity enhancement due to branching with a measurable feature of polymer chain like hyperbranch content.

Appendix A3

Results from blends of linear and branched model polyethylene resins (including the 3-arm star resins in chapter IV) are shown. The results explain how the new quantities to quantify branching from the scaling/SANS approach vary in blends of polyethylene.

Appendix A4

A primary goal while developing the scaling/SANS approach was to provide sufficient quantification of a branched polymer that can be used to illustrate the polymer chains in a melt/matrix. In this appendix, polyethylene resins from various catalyst systems are quantified and the polymer chain in each case is pictorially represented based on the measured branch contents. Such comprehensive quantification is able to provide catalyst chemists with an enhanced picture of the polymer that can help them better understand the effects of current catalyst systems and produce new catalyst systems to design different polyethylene structures.
I.6 References


CHAPTER II

Persistence Length of Short-Chain Branched Polyethylene*

Persistence Length of Short-Chain Branched Polyethylene

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II.1 Abstract

The effect of short-chain branching (SCB) on the persistence length \( l_p \) of polyethylene (PE) was studied using small angle neutron scattering (SANS). In thermodynamically good solvents, \( l_p \) can be measured directly from the scattering vector \( q_{tr} \) at the crossover from good solvent mass-fractal scaling to the rod-like persistent scaling, using the Unified Equation described in the text. The method was used to study \( l_p \) of both linear and branched PE in deuterated p-xylene, which is a good solvent for PE at 125 °C. The results indicate an increase in \( l_p \) of the backbone chain with increasing SCB content, independently measured using Fourier Transform Infrared Spectroscopy (FTIR). These results corroborate the behavior previously reported in Monte Carlo simulations of short-chain branched polymers. A functional relationship for \( l_p \) in terms of the number of SCBs is proposed.
II.2 Introduction

The molecular structure of a polymer is an important characteristic influencing physical properties. Branching in particular, plays a crucial role in defining the structure. Branching can be broadly classified as short-chain branching (SCB), referring to branches that have only a few carbon atoms and are much smaller than the backbone of the linear molecule to which they are attached, and long-chain branching (LCB) where the length of the branch is comparable to that of the backbone. SCBs arise during the production of commercial polyolefins such as linear low-density polyethylene (LLDPE) copolymers with butene, hexene or octene using either Ziegler-Natta or metallocene catalysts.\textsuperscript{1,2} These branches have a significant effect on the properties of polymers. For instance, the presence of a few SCBs can cause a change in crystallinity of melt crystallized polymers.\textsuperscript{3} They are known to effect properties such as density, rigidity, hardness and permeability.\textsuperscript{4} Further, the presence of these branches may also affect the rheological properties and hence the processability of these polymers.\textsuperscript{5-7} Such effects are often attributed to the change in chain structure due to branching.\textsuperscript{8} Due to the commercial importance of this class of polymers, a key objective has been to relate the change in the structure to the physical properties of the polymer chain.\textsuperscript{8} The examination of the local chain structure is important for such a correlation. Since the local chain persistence length, $l_p$, is indicative of the chain stiffness, a measure of $l_p$ is desired to study the effect of branching on the local chain structure. Recently, Monte Carlo simulations have suggested\textsuperscript{9-11} that the structural response of a polymer to short-chain branching is an increase in $l_p$. This paper focuses on the effect of short-chain branching on $l_p$ for polyethylene. Beaucage et al.\textsuperscript{12} have critically evaluated different methods to measure the persistence length from small angle scattering and the Unified Function\textsuperscript{13-15} used here is established as a useful method for such an analysis.
The persistent worm-like chain model, established by Kratky and Porod,\textsuperscript{16, 17} can be used to describe polymer chains with long-range and short-range interactions that cause them to have rigid back-bones and hence low flexibility. Kratky and Porod\textsuperscript{16, 17} introduced the concept of persistence length in their description of a worm-like chain. This length is a direct measure of the local chain conformation and quantifies the stiffness of a long polymer chain. The persistence length reflects the average projection of all the chain segments on a direction described by a given segment.\textsuperscript{12} The persistence length $l_p$ is defined by the orientation correlation function for a worm-like chain which follows an exponential decay.

$$
\langle \mathbf{t}(s_1) \cdot \mathbf{t}(s_2) \rangle = \langle \cos \psi \rangle = e^{-|s_2 - s_1|/l_p}
$$

where $\psi$ is the angle between the tangents $\mathbf{t}(s)$ to the chain at two points $s_1$ and $s_2$.

A polyethylene (PE) chain can be treated effectively using the Kratky-Porod worm-like chain model\textsuperscript{16, 17} for a persistent chain. Alternatively, in a freely jointed chain, rod-like segments each of length $l_k$, where $l_k$ is the Kuhn length,\textsuperscript{18} build up a polymer chain of mass-fractal dimension $d_f = 2$. Deviations from $d_f = 2$ are seen, for instance, in dilute solutions of polymer in good solvents. In this case, $d_f$ is seen to be approximately equal to 5/3.\textsuperscript{19} For a sufficiently long Gaussian chain, it can be shown that $l_k = 2l_p$\textsuperscript{20} The mass-fractal dimension $d_f$, radius of gyration $R_g$ and the persistence length $l_p$ of a polymer chain can be observed in a small angle scattering pattern and can be determined through the application of local scattering laws. For example, Guinier’s Law is given by,\textsuperscript{12-15, 21, 22}

$$
I(q) = G \exp \left( -\frac{q^2 R_g^2}{3} \right)
$$
where \( I(q) \) is the scattered intensity, scattering vector \( q = 4\pi \text{sin}(\theta/2)/\lambda \), \( \theta \) is the scattering angle, \( \lambda \) is the wavelength of radiation, \( R_g \) is the coil radius of gyration. \( G \) is defined as \( N_p n_p^2 \) where \( N_p \) is the number of polymer coils in given volume and \( n_p \) is a contrast factor equal to the excess number of electrons between the polymer coil and the solvent for x-ray scattering.

The mass-fractal power-law is another local scattering law, describing a mass-fractal object of dimension \( d_f \):\(^{12-15, 21}\)

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

where \( B_f \) is the power-law prefactor.\(^{15, 21}\) While Equation (2) gives an account of structural sizes \((R_g \text{ and } l_p)\), Equation (3) provides information about surface/mass scaling. In the Unified approach\(^{13-15}\), a structural level is defined by a Guinier regime and an associated power-law regime. Polymers display two structural levels, the overall radius of gyration \( R_g,2 \) and the substructural persistence length \( l_p \). Several studies\(^{12-14}\) have observed two power-law regimes for such systems, exhibiting structural limits at both high-\( q \) and low-\( q \). These limits are visible as regimes of exponential decay in Figure 1. A power-law regime of \(-5/3\) is expected at low-\( q \) and \(-1\) is expected at high-\( q \). This scaling behavior can be interpreted as mass-fractal scattering from a large-scale structure (of size \( R_g,2 \)) at the low-\( q \) power-law regime and mass-fractal (rod-like) scattering from small scale substructures (of size \( l_p \)) in the high-\( q \) power-law regime.
II.3 Materials and Methods

Short-chain branched samples of polyethylene were produced by a proprietary catalyst system in a continuous stirred tank reactor. Butene comonomer was used resulting in ethyl short-chain branches. The National Institute of Standards and Technology, Standard Reference Material, 1484 (NIST SRM 1484) was used as the linear standard for polyethylene. Samples are numbered 1-20 in order of increasing SCB content. Table 1 lists their weight-average molecular weight, $M_w$, polydispersity index ($M_w/M_n$), PDI, SCB content as number of SCB per 1000 main chain carbons, along with persistence length, $l_p$, and coil radius of gyration, $R_{g,2}$, the latter two measured using small angle neutron scattering (SANS). Samples were of variable LCB content. Long-chain branching affects the overall size and scaling of a polymer chain, observed at low-$q$ and does not affect the persistence length, a local feature observed at high-$q$. Thus the effect of SCBs on $l_p$ is independent of the presence of LCBs in the polymer. The LCB effects will be considered in a later publication.

Characterization of the samples for short-chain branch content (ethyl branches) was carried out using Fourier Transform Infrared Spectroscopy (FTIR). The technique characterizes branches qualitatively and quantitatively, by measuring the IR absorbance of the methyl, ethyl, butyl, isobutyl and hexyl branches in branched polyethylene samples. SANS was conducted on dilute solutions of polyethylene in deuterated p-xylene which is a good solvent for polyethylene at 125 °C. Standard 2mm path length quartz cells (banjo cells) were used. Deuterated p-xylene was purchased from Sigma-Aldrich. The polyethylene solutions were prepared by measuring a given quantity of the sample into the cell and transferring the deuterated solvent into the cell.
The cell was heated to 125 °C for 3 hours prior to the measurement and visually inspected before and after the run to ensure dissolution of the solute. The lack of evidence of any Porod scattering at low-$q$ and repeatability of the measurements after 6 hours at temperature confirms dissolution. 1 wt. % solution was used in each run to ensure dilute conditions. The dilute condition is determined by a concentration below the overlap concentration. The overlap concentration was determined from the molecular weight of the polymer by the method as described by Murase et al. To ensure that 1 wt. % was below overlap concentration, three different concentrations were examined: 0.25 wt. %, 0.5 wt. % and 1 wt. % for the highest molecular weight polymer sample. The data obtained corrected for concentration differences was superimposable demonstrating concentration below overlap. While weak virial effects were seen at the lowest $q$, they fell outside the range of data that were analyzed. Thus the coil radius of gyration remained unaffected for the different concentrations. The samples were run at 125 °C to maintain the solvated state. SANS experiments were conducted at the National Institute of Standards and Technology (NIST), Gaithersburg, NG-3 SANS, where the desired q-range was obtained using 3 sample-to-detector configurations (1m, 7m, 15m). A sample cell holder equipped with temperature regulation available at the beam line was utilized. Standard data correction procedures for background and incoherent scattering along with secondary standards were used to obtain $I(q)$ vs. $q$ in absolute units. Experimental runs took approximately 90 minutes per sample.
II.4 Results and Discussions

II.4.1 Unified Function

To describe the small angle scattering pattern of multiple structural levels that is observed in polymer melts and solutions, Beaucage\textsuperscript{13-15} has developed the Unified Function. The Unified Function has proved to be successful in describing various mass-fractal systems including polymers and ceramic aggregates.\textsuperscript{13-15, 25} The approach is able to describe the transition regime between structural levels and to determine the sizes involved in each level. It can be applied to dilute solutions of PE as described by Beaucage.\textsuperscript{12} Here, the method outlined in reference [12] is generalized to account for branching as described elsewhere.\textsuperscript{15, 21, 25, 26} For a Kratky/Porod worm-like persistent chain, displaying two levels of structure, the Unified Function is given as;\textsuperscript{12}

\[ I(q) = \left\{ G_2 e^{-q^2 R_{g2}^2}/3 + B_2 e^{-q^2 R_{g1}^2}/3 \left( q_{i}^* \right)^{-d_{j}/3} \right\} + \left\{ G_1 e^{-q^2 R_{g1}^2}/3 + B_1 \left( q_{i}^* \right)^{-1} \right\} \]

(4)

where \( q_{i}^* = \left[ \frac{q}{\text{erf}(qkR_{gi} / \sqrt{6})} \right] \) and \( k \approx 1.06 \)

In the above equation, the terms in the first bracket with subscript “2” represent the good solvent scaling regime with mass-fractal dimension \( d_{j2} \approx 5/3 \) and the second bracket with subscript “1” represent the rod-like persistent scaling regime. In each set of brackets, the first term gives the Guinier exponential decay and the second term yields the structurally limited power-law. \( G_2 \) is the Guinier prefactor, \( \text{erf} \) is the error function and \( R_{g2} \) is the coil radius of gyration for the mass-fractal regime, that is given by;\textsuperscript{14, 27}

\[ R_{g2}^2 = \frac{k n_k^{2/d_f} (2l_p)^2}{(c + 2/d_{\text{min}}) \left( 1 + c + 2/d_{\text{min}} \right)} \]

(5)
Where $k=1.75$ is a scaling constant for PE discussed below, $n_k$ is the number of Kuhn units, $c$ is the connectivity dimension and $d_{min}$ is the minimum dimension. Equation (5) differs from Equation (6) in reference [12] by accounting for deviation of the chain structure due to branching based on reference [15]. The power-law prefactor $B_2$ for the mass-fractal regime is given by:

$$B_2 = \frac{C_p d_{min} G_2}{R_{g2}^{d_{f2}/2}} \Gamma(d_{f2}/2)$$

(6)

where $\Gamma$ is the gamma function.

$C_p$ is a scattering polydispersity factor given by:

$$C_p = \frac{z_1}{z_2} \left( \frac{z_2 + z_{d_{f2}/2}}{z_2} \right)^{d_{f2}/2}$$

(7)

where $z_i$ is the $i^{th}$ moment of the molecular weight distribution. $C_p$ equals $M_z/M_w$ when $d_{f2}=2$. The Guinier prefactor for the rod-like persistent regime is given by:

$$G_1 = \frac{G_2}{n_k}$$

(8)

$R_{g1}$ and $B_1$ are defined for an infinitely thin rod of length $l_p$ as:

$$R_{g1} = \frac{l_p}{\sqrt{3}}$$

(9)

$$B_1 = \frac{\pi G_1}{2l_p}$$

(10)
The transition point $q_{tr}$ from the good solvent regime to rod-like persistent regime can be described as determined from a modified Kratky plot of $q^{d/2}I(q)$ vs. $q$,

i.e. $B_1 q_{tr}^{-1} = B_2 q_{tr}^{-d/2}$ at $q_{tr}$, \hspace{1cm} (11)

By substitution, this description of $q_{tr}$ can be extended to describe a branched mass-fractal polymer\textsuperscript{12} as;

\[
\frac{\pi G_1}{2l_p q_{tr}} = \frac{C_p G_2 d_{min} \Gamma\left(d_{f2}/2\right)(q_{tr})^{-d/2}}{R_{g2}^{d/2}} \hspace{1cm} (12)
\]

Substituting for $R_{g2}$, $G_2$ and $G_1$ from Equations (5) and (8), an expression for $l_p$ is obtained, given by;

\[
l_p = \left[ \frac{\Gamma\left(d_{f2}/2\right)d_{min} C_p}{\pi} \right]^{1/d_{f2}-1} \left[ (1/k)(c + 2/d_{min})(1 + c + 2/d_{min}) \right]^{d_{f2}/2d_{f2} - 2} \left[ 1/2q_{tr} \right] \hspace{1cm} (13)
\]

The SANS data, as shown in Figure 1, contains four distinguishable features, each of which provides two values associated with the $q$ and $I(q)$ positions of these features. At lowest $q$ we observe the plateau $I(q)$ value, and $R_{g2}$ for the coil. In the scaling regime, the slope and prefactor for the power-law decay are observed. Near the persistence length, a transition in slope is seen with corresponding $I(q)$ and $q$ values. At high-$q$ a power-law decay of -1 with a power-law prefactor is observed. These 8 observable features are modeled with a 5 parameter function where the variables that are floated while executing the Unified Fit are $C_p$, $d_f$, $R_{g2}$, $B_2$ and $B_1$. $d_{min}$ is held at 5/3 and $c = d_f / d_{min}$.\textsuperscript{15} $q_{tr}$ is obtained from Equation (11) which leads to $l_p$ from
Equation (13). The scaling constant $k = 1.75$ in Equation (5) was determined by comparing fit values with calculated values using Equations (5) and (13) for linear PE standards. For any sample analysis, the five-parameter Unified fit was robust with rapid convergence to the same values regardless of the starting parameters, as long as reasonable starting values are chosen. Reasonable starting values can be determined by visually inspecting the four main features of the scattering curve described above. The reported errors in values were propagated from the statistical errors in the data.

II.4.2 Determination of Persistence Length

Corrected SANS data in a log-log plot of $I(q)$ vs. $q$; are shown in Figure 1 for samples 1 and 14. The persistence length, $l_p$, was determined by fitting the data with Equation (4), represented by the solid curve in Figure 1. The dotted curves represent the Guinier exponential decay at low-$q$. The dashed curves represent the the persistence substructural level of the Unified Fit (second bracket in Equation (4) with subscript 1). This approach was carried out for linear and branched polyethylene with varying short-chain branch content. Linear polyethylene (NIST SRM 1484) displayed a persistence length of $6.5 \pm 0.8$ Å as shown in Figure 2. This matches the value that has been reported in literature, supporting the effectiveness of the current approach in determining persistence length.
Table 1 lists the samples that were examined along with the weight average molecular weight ($M_w$) as determined by GPC, polydispersity index (PDI), average radius of gyration of the coil ($R_{g,2}$) from SANS, SCB content ($n_{SCB}$), and the persistence length ($l_p$). Errors were propagated from the raw data. As seen from the plot of $l_p$ vs. $n_{SCB}$ in Figure 2, the persistence length of the polymer backbone increases with increasing short-chain branch content. This corroborates results from Monte-Carlo simulations$^{9, 10}$ of short-chain branched polymers. The increase in persistence length may be attributed to increased steric hindrance due to the presence of SCB’s.
Figure 1a. SANS data from short-chain branched PE. The slopes -5/3 and -1 indicate scaling at two separate structural regimes. Unified Fit is according to Equation (4). Data shown above was obtained at NIST. Sample PE – 1: Low short-chain branch content.
Figure 1b. SANS data from short-chain branched PE. The slopes -5/3 and -1 indicate scaling at two separate structural regimes. Unified Fit is according to Equation (4). Data shown above was obtained at NIST. Sample PE – 14: High short-chain branch content.
The persistence length is considered to display a value $l_p^0$ for no short chain branching, i.e. $n_{SCB} = 0$ and a value $l_p^\infty$ for a fully branched condition, i.e. $n_{SCB} \to \infty$. The difference, $\Delta$, of persistence length, $l_p$, at a given number of short chain branches per thousand carbons, $n_{SCB}$, from a fully branched condition is,

$$\Delta = l_p^\infty - l_p .$$

(14)

For an infinitesimal drop in the number of short chain branches, $-d(n_{SCB})$, a proportional change in the difference, $d\Delta$, is expected under a linear approximation. $d\Delta$ is also proportional to the difference, $\Delta$, since some clustering is expected for randomly arranged short chain branches. Clustered SCBs will not significantly affect $l_p$ compared to isolated SCBs. Thus, a diminishing return is expected on a given $d(n_{SCB})$ for smaller $\Delta$ (deviations from $l_p^\infty$). That is $d\Delta$ should scale with $\Delta$,

$$d\Delta = -\frac{\Delta \, dn_{SCB}}{\tau}$$

(15)

where $\tau$ is a constant of proportionality. Equation (15) can be integrated between $\Delta = l_p^\infty - l_p$ and $\Delta = l_p^\infty - l_p^0 = A$. This yields,

$$l_p = l_p^\infty - A \exp \left(-\frac{n_{SCB}}{\tau} \right)$$

(16)

$\tau$ can be described as the value of $n_{SCB}$ when $l_p = l_p^\infty - \frac{A}{e}$ and it controls the response rate of $l_p$ to $n_{SCB}$. 

42
Figure 2 shows a fit for the persistence length data with $l_p^\infty = 9.1 \pm 0.4 \, \text{Å}$, $A = 2.7 \pm 0.6$, $\tau = 3.4 \pm 1.7$ for the PE system. For a linear PE chain, $n_{SCB}$ is zero and Equation (16) gives $l_p \approx 6.5 \, \text{Å}$. On the other hand, for a theoretical PE chain with $n_{SCB} \to \infty$, i.e. all carbon atoms in the backbone are branched, Equation (16) gives $l_p \approx 9.1 \, \text{Å}$ as the upper limit for high degrees of short chain branching. The values of $l_p^\infty$, $A$ and $\tau$ can be considered as properties for commercial polyethylenes with ethyl branches. The effect of branch length will be investigated in a future publication for model polymer chains.

An increase in persistence length could lead to an increase in the coil radius of gyration ($R_{g2}$) for a given molecular weight. Although larger $R_{g2}$ are generally observed for higher SCB content in Table 1, a uniform increase is not seen in this set of samples due to the presence of variable low degrees of long chain branches and variable molecular weight. The low frequency of LCBs in the chains does not affect the persistence length. It is possible to characterize these samples for LCBs using SANS,\textsuperscript{15,25,26} which will be the focus of a future publication.\textsuperscript{†}

\[
\frac{dl_p}{dn_{SCB}} = -A \exp\left(-\frac{n_{SCB}}{\tau}\right) \frac{1}{\tau}
\]

(17)

\textsuperscript{†} Chapters III, IV and V extensively describe quantification of long-chain branching in polyethylene
Table 1. Persistence length for various short-chain branched polyethylene samples

<table>
<thead>
<tr>
<th>#</th>
<th>$M_w$</th>
<th>PDI</th>
<th>$R_g$</th>
<th>Persistence Length $l_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(g/mol)</td>
<td></td>
<td>(#/10$^3$C)</td>
<td>Å</td>
</tr>
<tr>
<td>1</td>
<td>86,000</td>
<td>8.1</td>
<td>1.3</td>
<td>112 ± 2</td>
</tr>
<tr>
<td>2</td>
<td>106,000</td>
<td>13.4</td>
<td>1.8</td>
<td>116 ± 2</td>
</tr>
<tr>
<td>3</td>
<td>111,000</td>
<td>10.1</td>
<td>2.5</td>
<td>130 ± 3</td>
</tr>
<tr>
<td>4</td>
<td>180,000</td>
<td>5.6</td>
<td>2.8</td>
<td>113 ± 2</td>
</tr>
<tr>
<td>5</td>
<td>147,000</td>
<td>5.5</td>
<td>2.8</td>
<td>141 ± 3</td>
</tr>
<tr>
<td>6</td>
<td>125,000</td>
<td>8.3</td>
<td>3.1</td>
<td>114 ± 2</td>
</tr>
<tr>
<td>7</td>
<td>120,000</td>
<td>6.0</td>
<td>3.2</td>
<td>134 ± 3</td>
</tr>
<tr>
<td>8</td>
<td>122,000</td>
<td>7.7</td>
<td>3.3</td>
<td>111 ± 2</td>
</tr>
<tr>
<td>9</td>
<td>127,000</td>
<td>5.4</td>
<td>3.3</td>
<td>100 ± 1</td>
</tr>
<tr>
<td>10</td>
<td>214,000</td>
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<td>3.3</td>
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</tr>
<tr>
<td>11</td>
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<td>3.7</td>
<td>125 ± 3</td>
</tr>
<tr>
<td>12</td>
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<td>3.7</td>
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</tr>
<tr>
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<td>3.5</td>
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</tr>
<tr>
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<td>6.6</td>
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</tr>
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<td>16</td>
<td>137,000</td>
<td>4.4</td>
<td>7.3</td>
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</tr>
<tr>
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<td>156 ± 4</td>
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<tr>
<td>20</td>
<td>127,000</td>
<td>5.8</td>
<td>12.1</td>
<td>127 ± 3</td>
</tr>
</tbody>
</table>
Figure 2. Persistence length $l_p$ plotted as a function of FTIR short-chain branch content. Fit is to Equation (16) as described in the text. $l_p = 6.5$ Å for the linear standard (NIST SRM 1484).
II.5 Conclusion

The persistence lengths of various polyethylene samples with variable SCB content, were determined by fitting small angle neutron scattering data with the Unified Equation. Variation of the persistence length with increasing short-chain branch content was studied and the results confirm a monotonic increase in persistence length with $n_{SCB}$ seen previously in simulation studies.\(^9,10\) The values obtained, ranged from 6.5 ± 0.8 Å (for linear polyethylene NIST SRM 1484) to 9.0 ± 0.60 Å for polyethylene with 12.1 branches per 1000 carbon atoms. A relationship between $n_{SCB}$ and $l_p$ is suggested which indicates a maximum enhancement of persistence length to 9.1 Å for fully branched PE. In forthcoming papers, we intend to explore this behavior for other polymer systems. In addition, the persistence length obtained using this approach will be used to calculate physical properties of branched polymers.\(^8,32\)

Acknowledgements

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II.6 References


CHAPTER III

Branch Content of Metallocene Polyethylene

III.1 Abstract

Small-angle neutron scattering (SANS) is employed to investigate the structure and long-chain branch (LCB) content of metallocene catalyzed polyethylene (PE). A novel scaling approach is applied to SANS data to determine the mole fraction branch content ($\phi_{br}$) of LCBs in PE. The approach also provides the average number of branch sites per chain ($n_{br}$) and the average number of branch sites per minimum path ($n_{br,p}$). These results yield the average branch length ($z_{br}$) and number of inner segments $n_i$, giving further insight into the chain architecture. The approach elucidates the relationship between the structure and rheological properties of branched polymers. This SANS method is the sole analytic measure of branch-on-branch structure and average branch length for topologically complex macromolecules.
III.2 Introduction

Structural branching is known to occur in a variety of materials such as polymers and ceramic aggregates.\textsuperscript{1, 2} Owing to the influence of branching on the physical and chemical properties of these materials, a universal technique to quantify the branch content has long been sought. Branching in polymers can be classified into short-chain branching (SCB), referring to branches that have only a few carbon atoms and are much smaller than the backbone to which they are attached, and long-chain branching (LCB) where the length of the branch is comparable to that of the backbone. The effects of short-chain branching have been discussed previously.\textsuperscript{3} A new scaling model\textsuperscript{4} has recently been developed to quantify long-chain branch content in such ramified structures. The scaling model has been employed successfully to study ceramic aggregates\textsuperscript{4} and to describe the folded and unfolded state in proteins and RNA.\textsuperscript{5} This model can be used to quantify long-chain branching in polymers as well. Long-chain branching has significant influence on the physical properties displayed by a polymer. The presence of long-chain branches (LCBs) considerably affects the structure and consequently the rheological properties and processability of polymers.\textsuperscript{6-9} Hence, an efficient and comprehensive method to quantify long-chain branch (LCB) content in polymers has been desired for many years. Various techniques based on size-exclusion chromatography (SEC),\textsuperscript{10} nuclear magnetic resonance (NMR) spectroscopy\textsuperscript{11} and rheology\textsuperscript{12, 13} have been utilized to determine LCB content in branched polymers. The drawbacks of these existing techniques have been previously discussed.\textsuperscript{14} SEC is ineffective in characterizing low levels of LCB. NMR cannot distinguish between short and long-chain branches and rheological estimates of LCB, though sensitive to low levels of LCB, tend to be semi-empirical and qualitative in nature.\textsuperscript{14} However, NMR is an effective technique to determine the total number of branch sites ($\beta$) in some polymer chains. In
this letter, a scaling model is applied to small angle neutron scattering (SANS) data obtained from dilute solutions of metallocene polyethylene samples, to quantify the LCB content in polymers. These samples have been previously studied in the literature. New data provided from this model will allow polymer chemists to better understand rheological consequences of polymer structures while developing new catalysts for complex polymer architectures.

A polyethylene (PE) chain can be considered to exhibit two structural levels, the overall radius of gyration \( R_g \) with mass fractal dimension \( d_f \) and the substructural rod-like persistence length \( l_p \) or Kuhn length \( l_k=2l_p \). These features can be observed in a small angle scattering pattern and can be determined through the application of local scattering laws and mass-fractal power laws under the Rayleigh-Gans approximation. Local scattering laws such as Guinier’s law and power laws describe these levels. Guinier’s law is given by,

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

where \( I(q) \) is the scattered intensity, scattering vector \( q = 4\pi sin(\theta/2)/\lambda \), \( \theta \) is the scattering angle, \( \lambda \) is the wavelength of radiation, \( R_g \) is the coil radius of gyration, \( G \) is defined as \( N_p n_p^2 \) where \( N_p \) is the number of polymer coils in given volume and \( n_p \) is square of the difference in neutron scattering length density between coil and solvent times the square of the volume of the coil.

The mass-fractal power law is another local scattering law.

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

It describes a mass-fractal object of dimension \( d_f \), where \( B_f \) is the power law prefactor. Together, they give an account of local features like size (\( R_g \) and \( l_p \)) and surface/mass scaling.
Unified Function developed by Beaucage,\textsuperscript{3, 17-19} used here, is useful to examine small angle scattering data from fractal structures with multiple structural levels such as carbon nanotubes\textsuperscript{20} and polyethylene.

Beaucage\textsuperscript{4} has described a scaling model which can be employed to quantify branch content in polymers. A branched polymer chain of size $R_g$ is considered to be composed of $z$ freely jointed Kuhn steps each of size $l_k$ as shown in Figure 1a. The structure of the branched polymer can further be decomposed into an average minimum path $p$ (number of Kuhn steps in the minimum path) through the structure as shown in Figure 1a. $p$ is an average traversing path through the chain structure. A scaling relationship can be proposed between $z$ and $p$,

\[ z = p^c = s^{d_{\min}} \tag{3} \]

where $c$ is the connectivity dimension assuming the scaling prefactor to be one. The minimum path $p$, is a mass-fractal of dimension $d_{\min}$ and size $r \sim p^{1/d_{\min}}$ while the total chain of $z$ Kuhn steps has a dimension $d_f \geq d_{\min}$ and the same size $r \sim z^{1/d_f}$. A parameter $s$ (eq. 3) can also be defined using $d_{\min}$ that reflects the number of steps required to connect all branch points and end points in the polymer structure by straight lines (size $r \sim s^{1/c}$). Substituting $p \sim r^{d_{\min}}$ in eq. 3 and comparing with $z \sim r^{d_f}$ yields $d_f = cd_{\min}$, which shows that the chain scaling $(d_f, z)$ can be decomposed into contributions from chain tortuosity $(d_{\min}, p)$ and chain connectivity $(c, s)$. For a linear polymer chain $d_{\min} = d_f$ and $c = 1$. On the other hand, for a completely branched object like a sphere or a disk, where a linear minimum path can be traversed, $d_f = c$ and $d_{\min} = 1$. The minimum path dimension, $d_{\min}$, and connectivity dimension $c$ represent different features of the branched chain. While $c$ increases with increased branching or connectivity, $d_{\min}$ increases with
tortuosity in the chain, driven by the thermodynamics in a dilute polymer solution. That is, for a linear chain in good solvent \( d_{\text{min}} = 5/3 \) and \( c = 1 \). For a branched chain, \( 1 < c \leq d_f \) and \( 1 \leq d_{\text{min}} \leq 5/3 \). \( d_{\text{min}} \) deviates from 5/3 because the minimum path can find shortcuts through the branched structure. From the scaling model, the mole fraction branches (\( \phi_{br} \)) is given by,

\[
\phi_{br} = \frac{z - P}{z} = 1 - z^{c-1}
\]  

(eqns. 1 and 2 can be used to calculate \( d_f, c, p \) and \( s \). \( d_{\text{min}} \) can be calculated from

\[
d_{\text{min}} = \frac{B_f \Gamma\left(\frac{d_f}{2}\right)}{C_p \Gamma\left(\frac{d_f}{2}\right) G} \tag{5}
\]

where \( C_p \) is the polydispersity factor and \( \Gamma \) is the gamma function. The quantities in eqns. 4 and 5 can be acquired from small angle neutron scattering (SANS) data from dilute hydrogenous polymer solutions in deuterated solvent fit to the Unified Function that is given by,

\[
I(q) = \left\{ \begin{array}{l} G_2 e^{-\left(q^2 R_{g2}^2\right)/3} + B_2 e^{-\left(q^2 R_{g1}^2\right)/3} q^d_{f2} \left( \frac{q^*}{q} \right)^k_f \left( \frac{q^*}{q} \right)^{d_{f2}} \\ G_1 e^{-\left(q^2 R_{g1}^2\right)/3} + B_1 \left( q^* \right)^{-1} \end{array} \right\}
\]  

where \( q^* \approx \frac{q}{\text{erf} \left( qkR_g / \sqrt{6} \right)} \) and \( k \approx 1.06 \)

The terms in the first bracket with subscript “2” represent the good solvent scaling regime with mass-fractal dimension \( d_{f2} \approx 5/3 \) and the second bracket with subscript “1” represent the rod-like persistent scaling regime. In each set of brackets, the first term gives the Guinier exponential decay and the second term yields the structurally limited power-law. The SANS data, as shown in Figure 2, contains four distinguishable features, each providing two values associated with the \( q \) and \( I(q) \) positions of these features. At lowest \( q \) we observe the plateau \( I(q) \) value, and \( R_{g2} \) for
the coil. In the scaling regime, the slope and prefactor for the power-law decay are observed. Near the persistence length, a transition in slope is seen with corresponding \( I(q) \) and \( q \) values. At high-\( q \) a power-law decay of -1 with a power-law prefactor is observed. These 8 observable features are modeled with a 6-parameter function where the variables that are floated while executing the Unified Function are \( C_p, d_f, R_g, B_2, d_{\text{min}} \) and \( B_1 \). All the parameters used in the Unified function have been described in detail previously.3,19

For a long-chain branched polymer, as shown Figure 1a, branch sites occur along the minimum path through the structure. The average minimum path is composed of segments between branch points or chain ends having an average number of Kuhn steps, \( (p/n_{s,p}) \), where \( n_{s,p} \) is the average number of segments per minimum path. The end-to-end distance of the minimum path, \( r \), in units of number of Kuhn steps can then be given by,

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

(7)

For a branched polymer chain, \( r \) can also be described in terms of \( p \) (Figure 1a) as

\[
r = p^{1/d_{\text{min}}}
\]  

(8)

Equating eqns. 7 and 8, we obtain the following relationship,

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

(9)

The number of branch sites per minimum path is then given by,
\[ n_{br,p} = n_{s,p} - 1 \]  \hspace{1cm} (10)

The average number of Kuhn steps in a segment, \( n_{k,s} \), can be described by,

\[ n_{k,s} = \frac{p}{n_{br,p} + 1} = \frac{z}{2n_{br} + 1} \]  \hspace{1cm} (11),

where \( n_{br} \) is the number of branch sites per chain, \( n_{br,p} + 1 \) is the number of segments in the minimum path and \( 2n_{br}+1 \) is the total number of segments in the polymer.

From eq. 3, we can rewrite eq. 11 as,

\[ n_{br} = \left( \frac{z \left( \gamma_{2\alpha} - \gamma_{2c} \right)^{(1-\gamma_{2c})}}{2} - 1 \right) \]  \hspace{1cm} (12)

This quantity is equivalent to the average number of branches per chain, \( \beta \), obtained from NMR.4, 14, 22

The mole fraction branch content, \( \phi_{br} \), combined with \( n_{br} \) can be used to estimate a new quantity, the weight average branch length \( (z_{br}) \), from the following relationship,

\[ z_{br} = \frac{z \phi_{br} M_{Kuhn}}{n_{br,p}} \]  \hspace{1cm} (13)

where \( M_{Kuhn} \) is the mass of one Kuhn step as determined from the Kuhn length, \( l_k = 2l_p \), of a polyethylene sample,3 which is \( l_k \times 13.4 \text{ g/mole/Å} \). The quantity \( n_{br} \) obtained from this analysis is compared with \( \beta \) obtained from NMR22.
Figure 1. (a) Schematic of a branched polymer: The polymer is composed of Kuhn steps of length $l_k$. The dark lines represent an average minimum path $p$ of dimension $d_{\text{min}}$. The lighter lines represent the long-chain branches (b) Connective path represented by straight lines connecting branch points and free ends (grey dots), of total size $s$ and connectivity dimension $c$. 
III.3 Materials and Methods

We used metallocene catalyzed model branched polyethylene chains with low degrees of structural branching and narrow molecular weight distributions (Table 1).

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>LCB/10³°C</th>
<th>$M_n$</th>
<th>PDI</th>
<th>$\beta$</th>
<th>$n_{br}$</th>
<th>$n_{br,p}$</th>
<th>$\phi_{br}$</th>
<th>$z_{br}$</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±1500</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±1600</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>16,500±1600</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±1700</td>
</tr>
</tbody>
</table>

These samples have been extensively studied and characterized in the literature. 12, 13, 22 SANS was performed on dilute solutions of these model polyethylenes in deuterated p-xylene which is a good solvent for polyethylene at 125°C. Deuterated p-xylene was purchased from Sigma-Aldrich. The samples were equilibrated at 125 °C for 3 hours prior to the measurements to ensure complete dissolution of the solute. 1 wt. % solutions were used, well below the overlap concentration as described by Murase et al. 23 as verified by superposition of concentration normalized data from 0.25 wt. %, 0.5 wt. % and 1 wt. % for the same polymer solution. SANS experiments were carried out at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory, Argonne and NG-7 SANS 24 at National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), Gaithersburg. Standard data correction procedures for transmission and incoherent scattering along with secondary standards were used to obtain $I(q)$ vs. $q$ in absolute units. 25 Experimental runs took approximately 4 hours per sample at IPNS and 2 hours at NIST.
III.4 Results and Discussions

Corrected SANS data is plotted in a log-log plot of $I(q)$ vs. $q$; as shown in Figure 2. The data is fit to the Unified Function (eq. 6)\textsuperscript{3, 17-19} followed by the application of the scaling model.\textsuperscript{4} The dotted curve in Figure 2 represents the Guinier exponential decay at low-$q$. The dashed curve in Figure 2 represents the Unified Fit at the persistence substructural level. As long as reasonable starting values are chosen, for each sample analysis, the Unified fit was robust with rapid convergence to the same values. Reasonable starting values can be determined by visually inspecting the four main features of the scattering curve, described above. Table 1 lists the sample names, NMR branch content in terms of number of long-chain branches per 1000 carbon atoms,\textsuperscript{22} LCB/10\textsuperscript{3}C, number average molecular weight\textsuperscript{22} $M_n$, polydispersity index ($M_w/M_n$),\textsuperscript{22} PDI and average number of branch sites per chain, $\beta$, from NMR.\textsuperscript{22} The NMR branch content, in terms of number of long-chain branches per 1000 carbon atoms, is converted to average number of branch sites per chain, $\beta$, using the relationship,\textsuperscript{22}

\[
\beta = \frac{(\#LCB/1000)_{NMR} M_n}{14,000}
\]

where, $M_n$ is the number average molecular weight of the polyethylene, and 14,000 g/mole refers to the molar mass of 1000 backbone carbons. Table 1 further lists the quantities calculated from SANS including number of branch sites per chain from eqns. 9 to 12, $n_{br}$, number of branch sites per minimum path from eqns. 9 and 10, $n_{br,p}$, mole-fraction branches from eq. 4, $\phi_{br}$, and average branch length from eq. 13, $z_{br}$. Table 2 lists the average radius of gyration of the coil ($R_g$), mass-fractal dimension, $d_6$, connectivity dimension, $c$, and persistence length,\textsuperscript{3} $l_p$, measured from SANS. Errors reported were propagated from counting the error the raw data.
Figure 2. SANS data for sample HDB-1 fit to the Unified fit\textsuperscript{17, 18}. Data shown above was obtained at IPNS.
Table 2. Size and dimensions of Dow HDB Samples measured from SANS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_g$ (Å)</th>
<th>$d_l$</th>
<th>$c$</th>
<th>$l_p$ (Å)</th>
</tr>
</thead>
<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>

Figure 3a plots $n_{br}$ calculated from eq. 11 against $\beta$ from ref. 22 with good agreement, although the value of $n_{br}$ is slightly higher than $\beta$. Figure 3b plots $n_{br,p}$ calculated from eq. 9 against $n_{br}$ from eq. 11. While $n_{br}$ measures every branch point in a polymer chain, $n_{br,p}$ reflects the number of branch points in the minimum path. For a comb or 3 arm star structure (top inset, Figure 3b), with no branch-on-branch structure, it is expected that $n_{br,p} = n_{br}$. For a more complex structure displaying branch-on-branch topology, $n_{br,p} < n_{br}$. Although we observe a monotonic relationship in the plot, $n_{br,p}$ is lower than $n_{br}$ for the HDB samples. This implies the presence of branch-on-branch architecture in these samples. The plot of $n_{br,p}$ versus $n_{br}$ in Figure 3b, shows a stronger deviation at higher branch content. The $n_{br,p}$ value plateaus at about 0.1 while $n_{br}$ increases to almost 0.3. The plateau in $n_{br,p}$ indicates that the minimum path branch content reaches a constant value while additional branches are added through branch-on-branch structures. The system consists of a few hyperbranched chains in a majority of linear chains at high branch content, rather than a uniform distribution of branching because $n_{br}$ is less than 1 and due to the noted difference between $n_{br,p}$ and $n_{br}$. 

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Figure 3a. Plot of number of branch sites per chain, $n_{br}$, calculated from eq. 12 against average number of branches per chain, $\beta$, from NMR.\textsuperscript{22} The dashed line represents $n_{br} = \beta$. 
Figure 3b. Plot of number of branch sites per minimum path, $n_{br,p}$, calculated from eq. 10 against $n_{br}$ calculated from eq. 12. The dotted line represents $n_{br} = n_{br,p}$. 
As mentioned earlier, the average branch length, $z_{br}$, can have significant impact in understanding the rheological behavior of long-chain branched polymers. Figure 4a shows a log-linear plot of the zero shear rate viscosity enhancement, $\eta_0/\eta_{0,L}$, as reported by Costeux et al.,\textsuperscript{22} versus the average branch length, $z_{br}$. An exponential increase in the viscosity enhancement with increasing branch length is observed.

The extrapolation of the fit of the data in Figure 4a intercepts the $z_{br}$ axis around 9,000 g/mole. This implies that the viscosity enhancement effect due to long-chain branching starts to occur, when the weight average branch length becomes 9,000 g/mole. For model samples with monodisperse branches,\textsuperscript{26} it has been previously reported that significant rheological affects are only observed for branches 2.4 times the entanglement molecular weight, $M_e$, of 1250 g/mole.\textsuperscript{13} Since $z_{br}$ is a weight-average branch length, the ratio of $z_{br}$ to the literature value\textsuperscript{26} suggests that the higher value in the current analysis can be attributed to the polydispersity in the branch lengths of the HDB samples. This implies a polydispersity index of $M_w/M_n \approx 9000/3000 = 3$ for the branches.\textsuperscript{†}

Based on previous studies,\textsuperscript{22,27} the viscosity enhancement can also be attributed to the number of inner segments per chain, $n_i$, as described in ref. 22, in branch-on-branch polymer chains. $n_i$ can be approximated by,

$$n_i = n_{br} - n_{br,p}$$ (12)

\textsuperscript{†} Refer to Addendum I in page 73 for additional discussion subsequent to publication.
Figure 4b shows a plot of viscosity enhancement, $\eta_0/\eta_{0,L}$, versus $n_i$ calculated in this way. The plot displays a linear increase in viscosity enhancement with increasing number of inner segments for the samples studied. If the inner segments are considered not to contribute to the viscous response of the melt and since the mole fraction of inner segments in the melt is proportional to $n_i$, we can consider the polyethylene melt as a dilute solution of $n_i$ inner segments per chain in a melt of mostly linear polyethylene. The linear functionality of $\eta_0/\eta_{0,L}$ in $n_i$ is then analogous to a dilute suspension of particulates. We can use the Einstein approximation\textsuperscript{28} for a dilute particulate suspension, $\eta_0 = \eta_{0,L} \left(1 + n_i [\eta_0]\right)$ as an approximation, except that there is a shift of about 0.015 on the $n_i$ axis. Einstein behavior indicates that inner segments do not contribute to flow, acting as particulate inclusions, and show a simple volumetric exclusion from the remaining viscous material composed of linear chains and non-hyperbranched chains. In the Einstein linear equation the slope, 278 chains/inner segment, corresponds to a type of intrinsic viscosity for hyperbranched-structures in a suspension of linear chains. The shift factor of 0.015 inner segments/chain may arise due to the presence of a small population of branched segments that are not long enough to significantly affect viscosity. These are reflected in Figure 4a by the non-zero intercept on the $z_{br}$ axis.
Figure 4a. Log-linear plot of zero shear rate viscosity enhancement for linear polyethylene of the same $M_w^{22}$ against the average length of a branch, $z_{br}$ (from SANS), for the HDB samples. The extrapolation of $z_{br}$ data intercepts the $z_{br}$ axis at 9000 g/mole.
Figure 4b. Linear plot of zero shear rate viscosity enhancement for linear polyethylene of same $M_w^{22}$ against number of inner segments per chain, $n_i$, for the HDB samples. The error in $n_i$ for HDB-1 is smaller than the point size.
III.5 Conclusion

A novel scaling approach to characterize long-chain branch content in polyethylene has been presented. Through this approach, the new quantities mole fraction branch content, $\phi_{br}$, number of branch sites per chain, $n_{br}$, number of branch sites per minimum path, $n_{br,p}$, number of inner segments per chain, $n_i$, and average branch length, $z_{br}$, are reported. While $\phi_{br}$ quantifies the mole fraction long-chain branch content $z_{br}$ can provide additional information about the architectural makeup of a polymer resulting in improved understanding of its rheological properties. $n_{br,p}$ when combined with $n_{br}$ gives further details about the chain architecture. This information will give polymer and catalyst chemists enhanced information to understand polymer architectures with desirable rheological properties. The approach encompasses both qualitative and quantitative analysis of long-chain branching in polyethylene. The scaling model has been successfully employed previously to determine branching in ceramic aggregates$^4$ and to quantify the degree of folding in proteins and RNA.$^5$

The procedure described in this paper does have certain limitations. First, the system being studied would need to show mass-fractal scaling so it may not be applicable to some densely branched dendritic macromolecules for example. The method is also not able to give a firm value for the length at which a branch becomes a long-chain branch since there may be an overlap regime where both persistence affects associated with SCB (as discussed in ref. 3) and scaling affects associated with LCB are observed. The effect of polydispersity in polymers and blending of different systems can be accommodated in this approach and will be discussed in forthcoming papers. The new scaling approach discussed here, will be further tested with model star and comb polyethylene samples.
Acknowledgements

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III.6 References


Addendum I

Molecular weight distribution of long-chain branches in metallocene based polyethylene

In the scaling approach\textsuperscript{1, 2} long-chain branch content (and average LCB length) is estimated based on an average minimum path (short-circuit path) through the structure. One instance of this minimum path is represented in Figure 1a (page 76). So the average long-chain branch content, $\phi_{br}$, and average LCB length, $z_{br}$, that are measured from scaling/SANS, includes the hyperbranched segments that are part of the branches.

The Dow HDB metallocene PE (mPE) resins described in Fig. 4a (page 85) have a polydispersity index, $(M_w/M_n)_{\text{poly}} \sim 2$. As outlined by Soares\textsuperscript{3}, the mechanism that incorporates LCB in mPE’s implies that the polydispersity in long-chain branches, $(M_w/M_n)_{\text{LCB}}$, is expected to be the same as $(M_w/M_n)_{\text{poly}}$. In the description based on the scaling model\textsuperscript{1, 2}, this will be expected when no branch-on-branch structures are present. Hyperbranching can occur, albeit at low levels, for instance when macromonomers insert into a branched polymer chain (as observed for the Dow HDB series). As a result, the average branch length, $z_{br}$, from the scaling approach (that includes the hyperbranched segments) is higher than the average length of a non-hyperbranched LCB. This may be the reason why the $(M_w/M_n)_{\text{LCB}}$ predicted from the scaling model analysis is higher.

CHAPTER IV

Quantification of Branching in Model 3-arm Star Polyethylene*

Quantification of Branching in Model 3-arm Star Polyethylene

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IV.1 Abstract

The versatility of a novel scaling approach in quantifying the structure of model well-defined 3-arm star polyethylene molecules is presented. Many commercial polyethylenes have long side branches, and the nature and quantity of these branches varies widely among the various forms. For instance, low-density polyethylene (LDPE) is typically a highly branched structure with broad distributions in branch content, branch lengths and branch generation (in hyperbranched structures). This makes it difficult to accurately quantify the structure and the inherent structure-property relationships. To overcome this drawback, model well-defined hydrogenated polybutadiene (HPB) structures have been synthesized via anionic polymerization and hydrogenation to serve as model analogs to long-chain branched polyethylene. In this article, model 3-arm star polyethylene molecules are quantified using the scaling approach. Along with the long-chain branch content in polyethylene, the approach also provides unique measurements of long-chain branch length and hyperbranch content. Such detailed description facilitates better understanding of the effect of branching on the physical properties of polyethylene.
IV.2 Introduction

The molecular structure of commercial polyethylenes varies widely among the several forms that have proven useful in the marketplace. In particular, the levels and types of long-chain branching vary greatly. One finds nearly linear structures to low levels of long-chain branching in linear-low density polyethylene (LLDPE) and high density polyethylene (HDPE). Higher levels of long-chain branching is seen in low density polyethylene (LDPE). Long-chain branching in polyethylene is known to have significant effects on its chain dimensions and physical properties.\(^1\)\(^-\)\(^3\) For instance, the presence of long-chain branches in low-density polyethylene (LDPE) significantly improves its processability. In order to quantify the branch content in polyethylene, techniques such as size exclusion chromatography (SEC), nuclear magnetic resonance (NMR) spectroscopy, light scattering, and rheological measurements are frequently employed. Essentially, these techniques measure the number-average long-chain branches per chain, which is not sufficient to provide a detailed description of the structure of polyethylene.\(^4\)\(^-\)\(^6\) Moreover, the limitations of these techniques lead to incomprehensive quantification of branching. For instance while SEC is ineffective in measuring low levels of branching,\(^4\) NMR is unable to distinguish between branches exceeding six carbon atoms in length.\(^7\) A novel scaling approach has been developed recently to quantify the branch content in ramified structures such as polyethylene.\(^8\) The scaling model,\(^4\)\(^,\)\(^8\) when applied to small-angle neutron scattering (SANS) data, can quantify both short-chain branching\(^9\) and long-chain branching in polyethylene.\(^5\) Results obtained from this approach can complement analysis performed by other techniques such as those mentioned above.\(^5\)\(^,\)\(^6\) The scaling approach has been used previously to characterize other ramified materials such as ceramic aggregates,\(^8\) proteins,\(^10\) hyper-branched polymers\(^11\) and cyclic polymers.\(^12\)
LDPE is an industrially important polyethylene and typically displays broad distributions in molecular weight, branch content and branch length. Hence it is difficult to get an accurate quantification of the nature of the long-chain branching and its effect on physical properties. To better understand the structure-property relationships due to the presence of long-chain branches, it is desirable to have model structures with a low polydispersity index as well as controlled levels of branch content and branch length. Anionic polymerization is one of the most useful techniques in synthesizing polymers having precisely controlled structures. This form of living polymerization is characterized by its rapid initiation step and elimination of chain transfer and termination reactions that results in nearly monodisperse polymers. While it is not possible to synthesize polyethylene directly by this technique, it is possible to synthesize model polybutadiene that can be hydrogenated to eliminate unsaturation and form analogs of polyethylene. Polybutadiene synthesized by anionic polymerization have cis, trans and vinyl double bonds incorporated in the structure. Upon hydrogenation, the cis and trans double bonds are removed while the vinyl double bonds result in ethyl short-chain branches. Long-chain branched polybutadiene can be prepared using chlorosilane condensation chemistry. 

Hadjichristidis et al. have synthesized a variety of model branched polyethylene analogs by hydrogenating branched polybutadienes. These include polyethylene with 3-arm star, comb, H, pom-pom as well as dendritic architectures. In this article, the aforementioned scaling approach is applied to quantify the structure of model 3-arm star polyethylene synthesized by Hadjichristidis et al. The versatility of the scaling approach is highlighted here by presenting the detailed quantification of such model branched polyethylene resins.
IV.3 Scaling Model

Polyolefins like polyethylene (PE) in dilute solution display two structural levels: the average chain size $R$ with mass-fractal dimension $d_f$ and an average substructural rod-like persistence unit of length $l_p$ \(^1\) or Kuhn length $l_k \approx 2l_p$.\(^{19}\) These structural levels are observed in small-angle scattering patterns from polyethylene. The Unified Function\(^5, 6, 8, 9, 20, 21\) used in this article is useful in quantifying these structural levels in terms of their size and associated mass-fractal dimensions. A branched polymer like polyethylene can be described in terms of two distinct features. One is a short circuit path through the branched structure that displays an average tortuosity linked to the thermodynamic conditions and steric constraints. The other is an average connectivity based on the branch content, which is invariant to changes in thermodynamic conditions. These two average features of branched polymers can be described using a universal scaling model.\(^8\) The scaling model has been used previously in describing the structure and quantifying the topology of a variety of mass-fractals.\(^4, 5, 8-12\)

Considering a polyethylene chain of end-to-end distance $R$ and mass-fractal dimension $d_f$ composed of $z$ Kuhn steps of size $l_k$ (see Figure 1), the scaling model describes an average short-circuit path or minimum path $p$ with mass-fractal dimension $d_{\text{min}}$. The tortuosity in the polyethylene chain is described by $p$ and $d_{\text{min}}$. The connectivity of the polyethylene chain can be described by a connecting path $s$ with an associated connectivity dimension, $c$, that is obtained by joining chain ends and branch points with straight lines. $z$, $p$ and $s$ can be related to the chain size $R/l_k$ by,

\(^1\) Additionally, a dynamic size close to $l_p$ called the packing length [3] can be defined which is not discussed here.
A scaling relationship between $z$, $p$, and $s$ can then be derived as,$^5, 8$

$$z = \left( \frac{R}{l_0} \right)^{d_f}, \quad p = \left( \frac{R}{l_0} \right)^{d_{\text{min}}} \quad \text{and} \quad s = \left( \frac{R}{l_0} \right)^c$$  \hspace{1cm} (1)

From Eqs. 1 and 2 a simple relationship is obtained, $d_f = cd_{\text{min}}$, that shows how chain scaling is described via contributions from tortuosity and connectivity. For regular objects like rods and discs that are completely connected and have no tortuosity through the structure, $d_f = c$ and $d_{\text{min}} = 1$. $d_{\text{min}}$ increases with tortuosity, $c$ increases with increased connectivity. Thus for linear polyethylene in a good solvent, $d_f = d_{\text{min}} \approx 5/3$ and $c = 1$. For branched polyethylene in a good solvent, $d_f > d_{\text{min}}$, $1 < c \leq d_f$ and $1 \leq d_{\text{min}} \leq 5/3$.

In the scaling approach,$^4-6, 8$ to describe a branched polymer chain of molecular weight $z$, we define a minimum path, $p$, which is the molecular weight of the short-circuit path taken through the polymer chain from one end to another. The part of the molecule outside of the minimum path, $z-p$, is then considered to be as branches. Thereby, the mole fraction long-chain branch content, $\phi_{br}$, is obtained by,

$$\phi_{br} = \frac{z - p}{z} = 1 - z^{\frac{1}{c} - 1}$$  \hspace{1cm} (3)
Figure 1. Schematic of a 3-arm star polymer in the scaling model. Each Kuhn step is represented by a bead. The polymer of mass-fractal dimension $d_f$ is composed of $z$ Kuhn steps of size $l_k$. The dark beads represent a minimum path $p$ of dimension $d_{\text{min}}$, composed of 2 arms. The lighter Kuhn steps depict the long-chain branch which is the third arm. The dotted lines represent the connective path of length $s$ and dimension $c$. The chains are depicted in a non-overlapping extended conformation in order to distinguish the arms.
The calculation of branch fraction for symmetric stars is trivial and can be calculated by \( \phi_{br} = \frac{f - 2}{f} \), where \( f \) is the functionality of the symmetric star. For asymmetric stars, 3 different minimum paths (short circuits) are possible through the structure. The average minimum path can then be calculated as a weight-average moment of this path. For the model star polyethylene in this paper, where information about number of arms and arm lengths is available (see Table 2), an expression to obtain weight-average branch content is given by,

\[
\phi_{br,wt-avg} = \frac{\sum_{i=1}^{3} (z - p_i)^2}{\sum_{i=1}^{3} (z - p_i) z} \tag{3a}
\]

The Unified Function along with the scaling model when applied to scattering data from polyethylene provides substantial information to describe the topology of branched polyethylene. For example, the Unified Function in Eq. 4 gives \( R_{g2}, G_2, B_2, G_1, B_1 \) and \( d_f \).

\[
I(q) = \left\{ G_2 e^{-(qR_{g2}^2)/3} + B_2 e^{-q^2 R_{g1}^2/3} \left( q^* \right)^{-d_f/3} \right\} + \left\{ G_1 e^{-(q^2 R_{g1}^2)/3} + B_1 \left( q^* \right)^{-1} \right\} \tag{4}
\]

where \( q^* = \left[ \frac{q}{\text{erf}(q R_{g1} / \sqrt{6})} \right] \) and \( k \approx 1.06 \)

The terms in the first bracket with subscript “2” represent the overall chain size and the second bracket with subscript “1” represent the rod-like persistent scaling regime. The minimum dimension, \( d_{min} \), is calculated from these parameters and is given by,\(^5,8\)
\[ d_{\text{min}} = \frac{B_2 R_b^2}{C_p \Gamma \left( \frac{d_{\text{f}}}{2} \right) G_2} \]  

(5)

where \( C_p \) is the polydispersity factor\(^5,\ 9,\ 22\) and \( \Gamma \) is the gamma function. The weight-average number of Kuhn steps, \( z \), is given by the ratio of \( G_2 \) over \( G_1 \).\(^8,\ 9,\ 21\) The connectivity dimension, \( c \), is obtained from \( d_{\text{f}}/d_{\text{min}} \) as described in the scaling model. From the topological parameters obtained, an expression is derived\(^5\) for the weight-average number of branch sites per chain, \( n_{br} \), which is given by,\(^5\)

\[ n_{br} = \frac{z \left( \frac{5}{2} d_{\text{f}} - \frac{3}{2} c \right)^{\frac{1}{n_{br,p}}} - 1}{2} \]  

(6)

The weight-average \( n_{br} \) is comparable to the number of long-chain branches per chain that is obtained from NMR\(^5,\ 23\) for tri-functional branch points except that the NMR measurement is a number-average. The weight-average long-chain branch length, \( z_{br} \), is determined by,

\[ z_{br} = \frac{z \phi_{br} M_{\text{Kuhn}}}{n_{br,p}} \]  

(7)

where \( M_{\text{Kuhn}} \) is the mass of one Kuhn step and assuming \( f = 3 \) (branch site functionality). For polyethylene, \( M_{\text{Kuhn}} = 13.4 \ l_k \), where \( M_{\text{Kuhn}} \) has units of g/mole and \( l_k \) has units of Å.\(^5\) \( n_{br,p} \) represents the average number of branches per minimum path. Using \( n_{br} \) and \( n_{br,p} \), an expression for the hyperbranch content in terms of the average number of inner segments per chain, \( n_i = n_{br} - n_{br,p} \) is obtained.\(^5\) Inner segments refer to segments in a polymer that have branch points at both ends.
The well-controlled, model, 3-arm star polyethylene resins analyzed in this article were derived by saturation of anionically synthesized polydienes\(^1,16\) and were the same resins used in an earlier work.\(^1\) The polymers were stored under conditions appropriate to avoid degradation by DJL. The resins included both symmetric (A\(_3\) type) and asymmetric 3-arm (A\(_2\)B) stars, where A and B represent the individual arms in the 3-arm star polyethylene. A detailed description of the synthesis of the polybutadiene precursors and the subsequent hydrogenation to obtain the polyethylene analogs are given elsewhere.\(^1\) These model polymers have been well studied and characterized in the literature.\(^1,2\) SANS was performed on dilute solutions of model 3-arm star hydrogenated polybutadiene in deuterated p-xylene which is a good solvent for polyethylene at 125\(^\circ\) C. 500 ppm of butylhydroxytoluene (BHT) was used as a stabilizer and dissolved in the solvent during sample preparation. BHT and deuterated p-xylene were purchased from Fisher Scientific. The samples were equilibrated at 125 \(^\circ\)C for 2 hours prior to the measurements to ensure complete dissolution of the polymer. The polymer solution was stirred by means of micro-magnetic stir bars to homogenize the solution prior to the measurement. 1 wt. \% solutions were used which is well below the overlap concentration\(^24\) for all fractions. SANS experiments were carried out at NG-7 SANS\(^25\) at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), Gaithersburg. Standard data correction procedures for transmission and incoherent scattering along with secondary standards were used to obtain \(I(q)\) vs. \(q\) in absolute units\(^26\). Experimental runs took approximately 2 hours per sample.
IV.5 Results and Discussions

The corrected SANS data for the 3-arm star polyethylenes were plotted in log-log plots of \( I(q) \) vs. \( q \) and fit to the Unified Function in Eq. 4 followed by the application of the scaling model. Table 1 lists the sample names along with weight-average molar mass, \( M_w \), and polydispersity index, PDI, measured from SEC-MALLS.\(^1\) Table 1 also lists the quantities estimated from SANS and the scaling model that include weight-average molar mass, mole-fraction long-chain branch content, \( \phi_{br} \), from Eq. 3, number of long-chain branch sites per chain, \( n_{br} \), from Eq. 6, average long-chain branch length, \( z_{br} \), from Eq. 7 and number of inner segments per chain, \( n_i \), that was estimated as described in reference [5]. \( n_i \) is a measure of the hyperbranch content in a polymer chain.\(^5\) The last column in Table 1 lists the measured steric interaction in the 3-arm star polymers, \( \phi_{si} \), which is described later in this article. The errors reported were propagated from the data.

### Table 1: SANS characterization of model 3-arm star polyethylene resins

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M_w ) (kg/mol)(^a)</th>
<th>PDI ((M_w/M_n))^a</th>
<th>( M_w ) (kg/mol)(^b)</th>
<th>( \phi_{br} )</th>
<th>( n_{br} ) (kg/mol)</th>
<th>( z_{br} ) (kg/mol)</th>
<th>( n_i )</th>
<th>( \phi_{si} ) (kg/mol)</th>
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</thead>
<tbody>
<tr>
<td>PES(50)(_2)(5)</td>
<td>130</td>
<td>1.03</td>
<td>135±10</td>
<td>0.42±0.02</td>
<td>1.21±0.05</td>
<td>47±5</td>
<td>0.23±0.09</td>
<td>0.033±0.005</td>
</tr>
<tr>
<td>PES(50)(_2)(15)</td>
<td>138</td>
<td>1.04</td>
<td>135±8</td>
<td>0.40±0.02</td>
<td>0.93±0.04</td>
<td>54±5</td>
<td>0.22±0.08</td>
<td>0.026±0.005</td>
</tr>
<tr>
<td>PES(50)(_2)(25)</td>
<td>131</td>
<td>1.06</td>
<td>134±9</td>
<td>0.42±0.02</td>
<td>0.97±0.04</td>
<td>49±5</td>
<td>0.26±0.08</td>
<td>0.027±0.005</td>
</tr>
<tr>
<td>PES(43)(_3)</td>
<td>133</td>
<td>1.13</td>
<td>135±9</td>
<td>0.34±0.01</td>
<td>0.76±0.03</td>
<td>44±4</td>
<td>0.10±0.05</td>
<td>0.026±0.006</td>
</tr>
<tr>
<td>PES(15)(_2)(85)</td>
<td>129</td>
<td>1.17</td>
<td>128±13</td>
<td>0.61±0.03</td>
<td>1.88±0.07</td>
<td>66±6</td>
<td>1.00±0.12</td>
<td>0.034±0.005</td>
</tr>
<tr>
<td>PES(40)(_2)(60)</td>
<td>125</td>
<td>1.08</td>
<td>137±8</td>
<td>0.39±0.03</td>
<td>0.87±0.06</td>
<td>59±7</td>
<td>0.20±0.10</td>
<td>0.024±0.004</td>
</tr>
<tr>
<td>PES(27)(_3)</td>
<td>82</td>
<td>1.04</td>
<td>103±5</td>
<td>0.36±0.02</td>
<td>0.90±0.06</td>
<td>33±4</td>
<td>0.10±0.08</td>
<td>0.032±0.005</td>
</tr>
<tr>
<td>PES(53)(_3)</td>
<td>139</td>
<td>1.12</td>
<td>132±7</td>
<td>0.34±0.02</td>
<td>0.81±0.05</td>
<td>49±6</td>
<td>0.08±0.06</td>
<td>0.025±0.005</td>
</tr>
<tr>
<td>PES(48)(_3)</td>
<td>138</td>
<td>1.21</td>
<td>146±7</td>
<td>0.35±0.01</td>
<td>0.80±0.06</td>
<td>51±4</td>
<td>0.11±0.08</td>
<td>0.024±0.004</td>
</tr>
</tbody>
</table>

\(^a\)measured by SEC-MALLS

\(^b\)measured by SANS.
Scattering techniques like light, x-ray and neutron scattering measure the weight-average molar mass, $M_w$, of polymers. In this paper, a number of quantities including $M_w$ are measured from SANS. The analysis of model 3-arm star polyethylene can allow us to verify if these quantities are weight-average. The molar mass of 3-arm star polyethylene resins were estimated from SANS using a method described by Boothroyd et al. Figure 2 plots the weight-average molar mass, $M_w$, obtained from SANS against weight-average molar mass, $M_w$, from SEC-MALLS. The data shows reasonable agreement between the molar mass measured from the two techniques (error bars are not available for SEC-MALLS values).

Figure 3 plots the mole-fraction branch content, $\phi_{br}$, from Eq. 3, obtained from SANS against $\phi_{br, wt-avg}$ obtained from Eq. 3a. In a previous study conducted on commercial linear low-density polyethylene fractions, mole-fraction branch content measured for the parent resin using the SANS-scaling approach was found to be in good agreement with corresponding weight-average values calculated by summing the contribution from individual fractions. In the current study, the good correlation between $\phi_{br}$ and $\phi_{br, wt-avg}$ seen in Figure 3 for the model long-chain branched polyethylene is compelling evidence that the branch fraction measured from the SANS-scaling approach is a weight-average quantity.
Figure 2. Plot of weight-average molar mass, $M_w$, obtained from SANS and weight-average molar mass, $M_w$, obtained from SEC-MALLS for 3-arm star polyethylenes.
Using the individual arm-lengths available in Table 2, it is possible to calculate the weight-average arm length, \( z_{br,wt-avg} \), for the model 3-arm star resins by,

\[
z_{br,wt-avg} = \frac{\sum_{i=1}^{3} (Arm_i)^2}{\sum_{i=1}^{3} (Arm_i)}
\]

Figure 4 plots the average branch length, \( z_{br} \), from Eq. 7, obtained from SANS versus weight-average arm length, \( z_{br,wt-avg} \), from Eq. 8. The good correlation seen in figure 4 substantiates that the average branch length measured from the SANS-scaling approach is a weight-average quantity.

**Table 2. Arm lengths for 3-arm star polyethylenes**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Arm 1 (kg/mol)</th>
<th>Arm 2 (kg/mol)</th>
<th>Arm 3 (kg/mol)</th>
<th>( z_{br,wt-avg} ) (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES(50)(_2)(5)</td>
<td>52</td>
<td>52</td>
<td>5.2</td>
<td>49.8</td>
</tr>
<tr>
<td>PES(50)(_2)(15)</td>
<td>52</td>
<td>52</td>
<td>15.5</td>
<td>47.3</td>
</tr>
<tr>
<td>PES(50)(_2)(25)</td>
<td>52</td>
<td>52</td>
<td>26</td>
<td>46.8</td>
</tr>
<tr>
<td>PES(43)(_3)</td>
<td>44.5</td>
<td>44.5</td>
<td>44.5</td>
<td>44.5</td>
</tr>
<tr>
<td>PES(15)(_2)(85)</td>
<td>15.5</td>
<td>15.5</td>
<td>88.5</td>
<td>69.6</td>
</tr>
<tr>
<td>PES(40)(_2)(60)</td>
<td>42</td>
<td>42</td>
<td>62</td>
<td>50.5</td>
</tr>
<tr>
<td>PES(27)(_3)</td>
<td>28</td>
<td>28</td>
<td>28</td>
<td>28</td>
</tr>
<tr>
<td>PES(53)(_3)</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>PES(48)(_3)</td>
<td>48</td>
<td>48</td>
<td>48</td>
<td>48</td>
</tr>
</tbody>
</table>
Figure 3. Plot of mole-fraction branch content, $\phi_{br}$, from Eq. 3, obtained from SANS versus the calculated weight-average branch content, $\phi_{br, wt-avg}$, from Eq. 3a for 3-arm star polyethylenes.
The SANS-scaling approach uniquely quantifies the average hyperbranch content in terms of the average number of inner segments, \( n_i \), in a hyperbranched polymer. Previously it was seen that \( n_i \) has significant impact on rheological properties such as the zero-shear rate viscosity enhancement in branched polyethylene.\(^5\) Table 3 lists the zero-shear rate viscosity and the zero-shear rate viscosity enhancement for certain 3-arm star polyethylenes where data was available in the literature.\(^2\) A linear polyethylene with similar weight-average molecular weight was chosen to determine the enhancement for the branched polymers. Figure 5 plots the hyperbranch content, \( n_i \), measured from SANS versus the zero-shear rate viscosity enhancement, \( \eta_0/\eta_{0,L} \). Almost all the resins show very low hyperbranch content and it can be concluded that the viscosity enhancement is primarily due to the presence of a branch. In the case of PES(15)\(_2\)(85), it is seen that the viscosity enhancement is much higher when compared to the other resins. Correspondingly, high hyperbranch content is also measured for this resin. While it is not expected that hydrogenated 3-arm star polybutadienes prepared using chlorosilane linking chemistry\(^1\) have any hyperbranching, the distinctly high viscosity enhancement (along with a measured \( n_{br} = 1.88 \pm 0.07 \)) for PES(15)\(_2\)(85) seems to indicate the presence of an additional hyperbranched arm (leading to an inner segment) in this resin. Additionally, considering the measured average branch length, \( z_{br} \), for PES(15)\(_2\)(85), it can be inferred that the additional arm is the smaller arm (15.5 kg/mole) of the asymmetric star. The results here suggest that hyperbranched chains may be present even in polymers synthesized using anionic chemistry and SEC-based characterization may not be sufficient to discern these branched structures. Recently, chromatographic techniques such as temperature gradient interaction chromatography (TGIC) have shown great potential in characterizing such complex structures.\(^{28,29}\) The scaling approach in this article can complement analysis from such specialized chromatographic techniques.
The enhancement of viscosity due to the presence of branches is multifaceted where the number, size and type of branch can affect the rheological behavior. However, at low levels of hyperbranching, there seems to be a linear relationship between zero-shear rate viscosity enhancement and the hyperbranch content ($n_i$) as observed previously. The data plotted in Figure 5 can be treated analogous to Figure 4b in reference [5]. We can consider the polyethylene melt as a dilute solution of hyperbranched segments in a melt of non-hyperbranched 3-arm star polyethylene. A linear functionality of $\eta_0/\eta_{0,L}$ in $n_i$ is then comparable to a dilute suspension of particulates. The Einstein solution viscosity equation\textsuperscript{30} for a dilute particulate suspension, $\eta_0=\eta_{0,L}(1+n_i[\eta_0])$, can be used as an approximation, except that there is a shift of 0.1 on the $n_i$ axis. We obtain a slope of 7,550 chains/inner segment corresponding to a type of intrinsic viscosity for hyperbranched structures in a suspension of non-hyperbranched chains. This slope is much higher than the 278 chains/inner segment observed previously for certain metallocene polyethylene.\textsuperscript{5} The higher slope can be explained due to the presence of the hyperbranched segments among pure branched 3-arm star chains rather than mostly linear chain as in the case of the metallocene polyethylene.\textsuperscript{5} The 3-arm stars dynamically interact to a greater extent than their linear analogues thereby amplifying the effect of inner segments.

**Table 3.** Zero-shear rate viscosity enhancement for 3-arm star polyethylenes\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta_0$ (Pa.S)</th>
<th>$\eta_0/ \eta_{0,L}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES(50)$_2$(5)</td>
<td>9.25x10$^5$</td>
<td>141</td>
</tr>
<tr>
<td>PES(50)$_2$(15)</td>
<td>8.56x10$^6$</td>
<td>1300</td>
</tr>
<tr>
<td>PES(50)$_2$(25)</td>
<td>2.28x10$^6$</td>
<td>347</td>
</tr>
<tr>
<td>PES(43)$_3$</td>
<td>5.70x10$^6$</td>
<td>866</td>
</tr>
<tr>
<td>PES(15)$_2$(85)</td>
<td>4.60x10$^7$</td>
<td>6990</td>
</tr>
<tr>
<td>PES(40)$_2$(60)</td>
<td>6.42x10$^6$</td>
<td>976</td>
</tr>
</tbody>
</table>

\textsuperscript{a}From reference [2]
Figure 4. Plot of average branch length, $z_{br}$, obtained from SANS using Eq. 7 versus the calculated weight-average arm length, $z_{br, wt-avg}$, from Eq. 8 for 3-arm star polyethylenes.
In general, for star polymers, the crowding of the arms can lead to steric interactions. Such steric effects are expected to be lowest for 3-arm stars and increase with higher number of arms. There are two effects of branching in star polymers. The mass fractal dimension $d_f$ and topological dimension $c$ increase since the structure contains more mass in the same volume and it achieves this through addition of topological complexity. At the same time, the arms are forced to become less convoluted (decrease in $d_{\min}$) to accommodate this increased topological complexity and increase in mass per volume. An analogy can be found in chains tethered to a surface where the chains tend to straighten out at high packing densities.\textsuperscript{31} There are limits to this behavior in star polymers as described in the Daoud-Cotton model\textsuperscript{32} where the macromolecule forms a 3-d core due to the high degree of topological constraint at high functionality. For low functionality we observe a steric interaction that serves to diminish $d_{\min}$.

In the scaling approach, for a linear polymer chain in a good solvent, $d_{\min} = 5/3$. For a theoretical star polymer with a large number of arms, the steric interaction will be at a maximum. At such a state, the polymer chains could be fully extended (rod like) with $d_{\min} = 1$. Using the limits of a linear chain and infinite-arm star, an expression can be obtained to quantify the steric interaction factor in a star polymer, $\phi_{si}$, that is given by,

$$\phi_{si} = \frac{S_{\text{observed}} - S_{\text{unperturbed}}}{S_{\text{extended}} - S_{\text{unperturbed}}} = \frac{z^{1/f_{\min}} - z^{3/5}}{z^1 - z^{3/5}}$$  \hspace{1cm} (10)
Table 1 lists the $\phi_{si}$ measured for dilute solutions of the 3-arm star polymers in a good solvent. As expected, the steric interaction is very low for these polymers. For the symmetric 3-arm star polymers, while the measured $\phi_{si}$ values do not show much variation, the data seems to suggest that the steric interaction increases with increasing average number of arms per chain, $n_{br}$ (see Table 1). Additionally, figure 6 shows a possible dependence of the steric interaction factor on the geometric mean arm length. Generally, intrachain interactions in a good solvent are described through the interaction parameter and crowding of arms also involves an enthalpic interaction. However, the structural transformation observed by changes in $d_{\text{min}}$ and quantified in $\phi_{si}$, reflect entropic changes in chain conformation associated with this enthalpic interaction. We have only observed the steric interaction in good solvent for dilute solutions. If we follow the tethered chain analogy then we would expect this steric effect to almost vanish at the theta temperature or in a melt.$^{31}$ We plan to investigate the steric interaction factor in the future using model star polymers with variable arm length, functionality and solvent quality.
Figure 5. Plot of the zero-shear rate viscosity enhancement, $\eta_0/\eta_{0,L}$, versus the hyperbranch content, $n_i$, measured from SANS for 3-arm star polyethylenes. A linear behavior is expected based on results shown in reference [5].
Figure 6. Plot of the steric interaction factor, $\phi_{si}$, versus the calculated geometric mean arm length for 3-arm star polyethylenes. Dotted line is a trend line.
IV.6 Conclusion

A novel scaling approach to quantify the topology of complex macromolecular structures has been presented in this article. The usefulness of the scaling approach in quantifying the branch content of model polyethylene resins was illustrated. Along with estimating the average number of long-chain branches per polymer chain, \( n_{br} \), the approach provides unique measurements of mole-fraction branch content, \( \phi_{br} \), average long-chain branch length, \( z_{br} \), hyperbranch content, \( n_i \), and steric interaction due to branching, \( \phi_{si} \). The measurements of \( \phi_{br} \) and \( z_{br} \) made via the SANS-scaling approach show good correlation with the calculated averages for these model 3-arm star resins. Additionally, the high viscosity enhancement in a particular 3-arm star resin was attributed to the presence of hyperbranched segments that was measured using the SANS-scaling approach. The example discussed in this article demonstrates how the detailed quantification available using the scaling approach can lead to better understanding of the effects of polymer structure on physical properties. The scaling approach can also be employed to quantify branching in other complex structures such as ceramic aggregates\(^8\), cyclic polymers\(^{12}\) and to quantify the degree of folding in proteins and RNA\(^{10}\).

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IV.7 References


CHAPTER V

Branch Length Distribution in TREF Fractionated Polyethylene*

Branch Length Distribution in TREF Fractionated Polyethylene

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V.1 Abstract

Commercial polyethylene is typically heterogeneous in molecular weight as well as in molecular topology due to variability in catalyst systems and catalyst activity. Further, processing of polyethylene after polymerization may also result in changes to the structure. While quantification of molecular weight is routine using gel permeation chromatography (GPC); quantification of the heterogeneity in molecular topology and microstructure is more difficult. In this paper, a novel method is used to examine the structure and branch content of a linear low density polyethylene (LLDPE). The method uses a scaling model to analyze small-
angle neutron scattering (SANS) data from dilute solutions of a series of LLDPE fractions. The scaling approach quantifies short-chain and long-chain branch content in polymers concurrently, thereby illustrating the distribution of these branches in the polyethylene fractions. Additionally, new quantities such as the average long-chain branch length and hyperbranch content are measured to provide further insight into the structure of these polymers. LLDPE used in this study is fractionated using temperature rising elution fractionation (TREF). Results from the analysis of these fractions show evidence of long-chain branching in commercial LLDPE which could be partly attributed to post-synthesis processing conditions.
V.2 Introduction

The presence of branching in polyethylene has significant impact on its physical properties. Both short-chain and long-chain branching levels affect properties such as density, crystallinity, strength and processability.¹⁻⁵ In the production of commercial polyethylene, a variety of catalysts are used in order to obtain desired levels of branching. The presence of a mixture of active sites paired with the reaction conditions lead to distribution in molecular weight and branching in polyethylene. For example, Ziegler-Natta catalysts are known to result in heterogeneity in short-chain branched polyethylene.⁶ Additional processing of polyethylene can affect the structure of the polymer as well. Common processing techniques such as extrusion, when air is not included, are thought to introduce low levels of long-chain branching in polyethylene that may result in unexpected physical properties.⁷,⁸ Characterization methods such as gel permeation chromatography (GPC) are routinely used to measure the distribution in molecular weights. On the other hand, quantification of molecular topology and distribution in branching is more difficult. While GPC, along with nuclear magnetic resonance (NMR) spectroscopy, light scattering and rheological measurements are frequently used to measure branching, drawbacks posed by these techniques lead to incomprehensive quantification. For instance, GPC is ineffective in measuring low levels of branching; NMR is unable to distinguish effectively between short-chain and long-chain branches once the branch length exceeds six carbon atoms in length.⁹
A novel scaling method\textsuperscript{10-13} has been developed to comprehensively quantify branching in polyethylene.\textsuperscript{12, 13} The model has been applied successfully to characterize other ramified materials such as ceramic aggregates\textsuperscript{10}, proteins\textsuperscript{14}, hyper-branched polymers\textsuperscript{15} and cyclic.\textsuperscript{16} In the context of polyethylene the scaling model\textsuperscript{10, 11}, when applied to small-angle neutron scattering (SANS) data, can quantify and distinguish between short-chain branching\textsuperscript{12} and long-chain branching\textsuperscript{13}; this allows for a complete analysis of branching. In this paper, the scaling model is applied to SANS data from a series of fractions of linear low density polyethylene (LLDPE). Preparative temperature rising elution fractionation (pTREF) was utilized to fractionate LLDPE\textsuperscript{17, 18} into fractions that were characterized by other techniques.

Linear low density polyethylene is essentially a copolymer of ethylene with $\alpha$-olefins such as butene, hexene and octene. Typically, commercial production of LLDPE utilizes heterogeneous multi-site Zeigler-Natta catalysts with varying comonomer concentration.\textsuperscript{6, 19, 20} Consequently these LLDPEs have a broad distribution in molecular weight and short-chain branch (SCB) content. In order to effectively study the structure-property relationships of such heterogeneous resins, it is necessary to fractionate LLDPE into components with narrower distributions of molecular weight and SCB content. Temperature rising elution fractionation (TREF) has gained significant attention in this regard. TREF is a technique that fractionates a semi-crystalline polymer according to molecular structure that affects crystallinity. Since SCB content directly impacts crystallinity of polyethylene, TREF can fractionate LLDPE based on the SCB content.\textsuperscript{6, 19-23}
V.3 Scaling Model

The molecular structure of polyolefins such as polyethylene (PE) in dilute solution displays two levels: the average coil size $R$ with mass-fractal dimension $d_f$, and an average substructural rod-like persistence unit of length $l_p$ or Kuhn length $l_k \approx 2l_p$. These structural features are observed in small-angle scattering patterns from polyethylene. The Unified Function used in this article is useful in quantifying such structural features. Considering a short-circuit path through a branched structure, macromolecules exhibit an average tortuosity in this short-circuit path linked to the thermodynamic conditions and steric constraints. Branched macromolecules also display an average connectivity based on the branch content. The connectivity is invariant to changes in thermodynamic conditions. These two average features of branched chains can be described using a universal scaling model. The scaling model has been useful in describing the structure and quantifying the topology of a variety of mass fractals.

For a polyethylene chain of end-to-end distance $R$ and mass-fractal dimension $d_f$ composed of $z$ Kuhn steps of size $l_k$ as shown in Fig. 1, the scaling model describes an average short-circuit path or minimum path $p$ with mass-fractal dimension $d_{min}$. $p$ and $d_{min}$ account for the tortuosity in the chain. The connectivity of the polyethylene chain can be described by a connecting path $s$ that is obtained by joining chain ends and branch points with straight lines. $z, p$ and $s$ can be related to the chain size $R/l_k$ by,

† Additionally, a dynamic size close to $l_p$, called the packing length [3] can be defined which is not discussed here.
where $c$ is the connectivity dimension. A scaling relationship between $z, p$ and $s$ can be expressed as

$$ z = p^c = s^{d_{\text{min}}} \quad (2) $$

Comparing equations (1) and (2) yields $d_f = cd_{\text{min}}$. For regular objects such as spheres and discs that are completely connected and have no tortuosity, $d_f = c$ and $d_{\text{min}} = 1$. While $d_{\text{min}}$ increases with tortuosity, $c$ increases with increased connectivity. So, for linear polyethylene in a good solvent, $d_f = d_{\text{min}} \approx 5/3$ and $c = 1$. For branched polyethylene in a good solvent, $d_f > d_{\text{min}}$, $1 < c < d_f$ and $1 \leq d_{\text{min}} \leq 5/3$. As described earlier, long-chain branching affects the overall size and scaling of the polyethylene chain, whereas short-chain branching affects the persistence length of polyethylene. The mole fraction long-chain branch content can be obtained by

$$ \phi_{br} = \frac{z - p}{z} = 1 - z^{c - 1} \quad (3) $$

The Unified Function along with the scaling model when applied to scattering data provides a plethora of information to describe the topology of branched polyethylene. For instance, the Unified Function in equation (4) gives $R_{g2}, G_2, B_2, G_1, B_1$ and $d_f$.

$$ I(q) = \left\{ G_2 e^{-\left(\frac{q^2 R_{g2}}{3}\right)} + B_2 e^{-\left(\frac{q^2 R_{g2}}{3}\right)} \left( q^* \right)^{-d_f/3} \right\} + \left\{ G_1 e^{-\left(\frac{q^2 R_{g1}}{3}\right)} + B_1 \left( q^* \right)^{-1} \right\} \quad (4) $$
\[ q_i^* = \left[ \frac{q}{\text{erf} \left( qkR_g / \sqrt{6} \right)} \right] \]

where \( k \approx 1.06 \) and \( q \).

The minimum dimension, \( d_{\text{min}} \), is calculated from these parameters and is given by \(^{10, 13}\)

\[ d_{\text{min}} = \frac{B_2 R_g}{C_p \Gamma \left( \frac{d_f}{2} \right) G_2} \quad (5) \]

where \( C_p \) is the polydispersity factor \(^{12, 13, 27}\) and \( \Gamma \) is the gamma function. The weight average number of Kuhn steps, \( z \), is given by the ratio of \( G_2 \) over \( G_1 \). \(^{10, 12, 26}\) The connectivity dimension, \( c \), is obtained from \( d_f d_{\text{min}} \) as described in the scaling model. From the topological parameters obtained, an expression is derived \(^{13}\) for the weight average number of branch sites per chain, \( n_{\text{br}} \), which is given by \(^{13}\),

\[ n_{\text{br}} = \left( \frac{z \left( \frac{5z}{2d_f} - \frac{3z}{2c} \right) \left( \frac{1}{1} \right)}{2} - 1 \right) \quad (6) \]

\( n_{\text{br}} \) is equivalent to the number of long-chain branches per chain that is obtained from NMR \(^{13, 28}\) for tri-functional branch points except that the NMR measurement is a number average. The mole fraction branch content, \( \phi_{\text{br}} \), along with \( n_{\text{br}} \) are used to determine the weight-average long-chain branch length, \( z_{\text{br}} \), from \(^{13}\),

\[ z_{\text{br}} = \frac{z \phi_{\text{br}} M_{\text{Kuhn}}}{n_{\text{br}}} \quad (7) \]
where $M_{\text{Kuhn}}$ is the mass of one Kuhn step and assuming $f = 3$ (branch site functionality). For polyethylene, $M_{\text{Kuhn}} = 13.4 \ l_k$, where $M_{\text{Kuhn}}$ has units of g/mole and $l_k$ has units of Å. With respect to short-chain branched polyethylene with ethyl SCBs, it was previously shown that\textsuperscript{12},

$$l_p = l_p^\infty - A \exp\left(\frac{-n_{\text{SCB}}}{\tau}\right)$$

(8)

where $l_p^\infty = 9.1 \pm 0.4$ Å is the persistence length of a fully short-chain branched polyethylene, $n_{\text{SCB}}$ is the number of short-chain branches per 1000 carbon atoms, $A = 2.7 \pm 0.6$ Å and $\tau = 3.4 \pm 1.7$ for polyethylene. The LLDPE used in the current study (PE-1) was produced with 1-hexene comonomer resulting in butyl short-chain branches. The effect of butyl SCBs on the relationship described in equation (8) is described later in this article.

V.4 Experimental

V.4.1 Temperature Rising Elution Fractionation

Temperature rising elution fractionation (TREF) is an established method that has proven valuable in the analysis of semi-crystalline polyolefins such as polyethylene and polypropylene.\textsuperscript{6, 19-23} TREF separates polymer molecules based on their melting point as controlled by short-chain branching. TREF has been particularly useful in analyzing conventional linear low-density polyethylene (LLDPE) grades produced with heterogeneous Ziegler-Natta catalysts due to their broad distributions in short-chain branch (SCB) content.\textsuperscript{6, 19-21} Basically, the TREF process consists of two steps: crystallization followed by elution. During the crystallization step, the polymer in dilute solution is cooled slowly (typically 5°C/hr and lower). Chains with low SCB content crystallize at higher temperatures. The elution step involves passing a good solvent
through a column that is packed with the crystallized polymer mixture. The temperature of the solvent is increased step-wise, thereby eluting polymer fractions in the reverse order from which they precipitated. In preparative TREF, the fractions are collected at different elution temperature intervals for further analysis. A detailed review of TREF and the theory behind the separation has been discussed in the literature. The weights of the fractions collected (98% recovery after fractionation) and their respective elution temperatures are listed in Table 1.

Table 1

SANS characterization of LLDPE fractions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight</th>
<th>Elution temp.</th>
<th>$M_w$</th>
<th>PDI</th>
<th>$l_p$</th>
<th>$n_{SCB}$ (NMR)</th>
<th>$\phi_{br}$</th>
<th>$n_{br}$</th>
<th>$z_{br}$</th>
<th>$n_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>°C</td>
<td>kg/m</td>
<td></td>
<td></td>
<td></td>
<td>#/1000 C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PE-1</td>
<td>15</td>
<td>- 98</td>
<td>4.6</td>
<td></td>
<td>7.7 ± 0.5</td>
<td>18.5</td>
<td>0.127 ± 0.040</td>
<td>0.130 ± 0.020</td>
<td>17 ± 1.6</td>
<td>0.050 ± 0.020</td>
</tr>
<tr>
<td>Frac 1</td>
<td>1.04</td>
<td>30 13</td>
<td>6.3</td>
<td></td>
<td>8.9 ± 0.7</td>
<td>64.8</td>
<td>0.022 ± 0.001</td>
<td>0.007 ± 0.003</td>
<td>8 ± 0.8</td>
<td>0.007 ± 0.003</td>
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<tr>
<td>Frac 2</td>
<td>0.68</td>
<td>50 36</td>
<td>4.6</td>
<td></td>
<td>8.8 ± 0.6</td>
<td>46.1</td>
<td>0.028 ± 0.002</td>
<td>0.013 ± 0.003</td>
<td>10 ± 0.8</td>
<td>0.007 ± 0.003</td>
</tr>
<tr>
<td>Frac 3</td>
<td>1.26</td>
<td>70 46</td>
<td>3.5</td>
<td></td>
<td>8.5 ± 0.6</td>
<td>35.6</td>
<td>0.057 ± 0.002</td>
<td>0.038 ± 0.005</td>
<td>12 ± 1.3</td>
<td>0.012 ± 0.005</td>
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<tr>
<td>Frac 4</td>
<td>0.65</td>
<td>80 78</td>
<td>3.0</td>
<td></td>
<td>8.5 ± 0.5</td>
<td>28.5</td>
<td>0.057 ± 0.003</td>
<td>0.039 ± 0.006</td>
<td>11 ± 1.1</td>
<td>0.012 ± 0.006</td>
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<td>1.57</td>
<td>85 83</td>
<td>2.7</td>
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<td>8.2 ± 0.5</td>
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<td>8 ± 0.8</td>
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<tr>
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<td>1.32</td>
<td>100 96</td>
<td>2.6</td>
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<td>7.9 ± 0.5</td>
<td>17.5</td>
<td>0.129 ± 0.005</td>
<td>0.113 ± 0.008</td>
<td>12 ± 1.1</td>
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<td>1.62</td>
<td>110 108</td>
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<td></td>
<td>7.0 ± 0.4</td>
<td>10.7</td>
<td>0.240 ± 0.010</td>
<td>0.149 ± 0.008</td>
<td>40 ± 1.5</td>
<td>0.149 ± 0.008</td>
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<tr>
<td>Frac 8</td>
<td>2.57</td>
<td>120 103</td>
<td>2.5</td>
<td></td>
<td>7.3 ± 0.5</td>
<td>5.9</td>
<td>0.153 ± 0.010</td>
<td>0.085 ± 0.007</td>
<td>9 ± 0.9</td>
<td>0.085 ± 0.007</td>
</tr>
<tr>
<td>Frac 9</td>
<td>1.43</td>
<td>125 118</td>
<td>1.9</td>
<td></td>
<td>7.0 ± 0.5</td>
<td>5.5</td>
<td>0.196 ± 0.040</td>
<td>0.122 ± 0.008</td>
<td>33 ± 1.5</td>
<td>0.110 ± 0.008</td>
</tr>
<tr>
<td>Frac 10</td>
<td>1.23</td>
<td>135 188</td>
<td>1.8</td>
<td></td>
<td>6.5 ± 0.4</td>
<td>3.9</td>
<td>0.295 ± 0.020</td>
<td>0.406 ± 0.050</td>
<td>60 ± 2.1</td>
<td>0.104 ± 0.053</td>
</tr>
<tr>
<td>Frac 11</td>
<td>1.28</td>
<td>150 245</td>
<td>1.7</td>
<td></td>
<td>6.6 ± 0.4</td>
<td>4.4</td>
<td>0.249 ± 0.008</td>
<td>0.155 ± 0.030</td>
<td>74 ± 2.3</td>
<td>0.155 ± 0.031</td>
</tr>
</tbody>
</table>
Figure 1. Schematic of a branched polymer according to the scaling model. Each Kuhn step is represented by a bead. The polymer of mass-fractal dimension $d_f$ is composed of $z$ Kuhn steps of size $l_k$. The dark beads represent the minimum path $p$ of dimension $d_{\text{min}}$. The lighter Kuhn steps symbolize the long-chain branches. The dotted lines represent the connective path of length $s$ and dimension $c$. 
V.4.2 Small-angle Neutron Scattering

SANS was performed on dilute solutions of LLDPE in deuterated p-xylene, which is a good solvent for polyethylene at 125° C. 500 ppm of butylhydroxytoluene (BHT) was used as a stabilizer and dissolved in the solvent during sample preparation. BHT and deuterated p-xylene were purchased from Fisher Scientific. The samples were equilibrated at 125 °C for 2 hours prior to the measurements to ensure complete dissolution of polyethylene. Additionally, the polymer solution was stirred by means of micro-magnetic stir bars to ensure proper mixing. 1 wt. % solutions were used, which is well below the overlap concentration\(^2^9\) for all fractions. SANS experiments were carried out at NG-7 SANS\(^3^0\) at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR), Gaithersburg and CG2 SANS in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL). Standard data correction procedures for transmission and incoherent scattering along with secondary standards were used to obtain \(I(q)\) vs. \(q\) in absolute units.\(^3^1\) Experimental runs took approximately 2 hours per sample at both facilities.

V.5 Results and Discussions

The corrected SANS data for the LLDPE fractions plotted in log-log plots of \(I(q)\) vs \(q\) were fit to the Unified Function in equation (4) followed by the application of the scaling model. Fig. 2 shows the SANS data and the associated Unified fit for Frac 11. The molecular weight of PE-1 and the fractions were estimated from SANS using a method described by Boothroyd et.al.\(^3^2\). The constant \(K\) in reference [32] accounts for the scattering contrast for the polymer in dilute
deuterated solvent and is a property of the polymer, solvent and type of radiation. For polyethylene in deuterated p-xylene, the constant $K$ was estimated to be $0.0012 \text{ mol cm}^2 \text{g}^{-2}$. NIST standard reference material 1484, a linear low-polydispersity standard, was utilized to determine $K$. Table 1 lists the quantities estimated from SANS and the scaling model that include persistence length, $l_p$, number of short-chain branches per 1000 carbon atoms, $n_{\text{SCB}}$ (from NMR), mole-fraction long-chain branch content, $\phi_{br}$, from equation (3), number of long-chain branch sites per chain, $n_{br}$, from equation (6), average long-chain branch length, $z_{br}$, from equation (7) and number of inner segments per chain, $n_i$, that was estimated as described in reference [13]. $n_i$ is a measure of the hyperbranch content in a polymer chain. The errors reported were propagated from the data.

V.5.1 Analysis of Moments

It is known that scattering techniques like x-ray, light and neutron scattering measure the second moment of molecular weight (weight-average molecular weight, $M_w$) of polymers. In this paper, a number of quantities including $M_w$ are measured from SANS. The analysis of the TREF fractions presents an opportunity to validate that these quantities measured are indeed weight-averaged quantities. The agreement between the SANS values and corresponding weight average values, $\Sigma w_j X_j$, calculated by summing the contribution from individual fractions, in Table 2 is good and is persuasive evidence that the SANS values are indeed weight-averaged values. $w_j$ is the ratio of the weight of each fraction to the total weight of the fractions collected. $X_j$ represents the quantities measured from SANS ($\phi_{br}$, $n_{br}$, $z_{br}$, $n_i$ and $l_p$) for each fraction. Small discrepancies
in Table 2 between the weight average values and the parent polymer values may be a result of incomplete recovery of the fractions from the TREF process.

Table 2

Analysis of moments from SANS

<table>
<thead>
<tr>
<th></th>
<th>$M_w$</th>
<th>$\phi_{br}$</th>
<th>$n_{br}$</th>
<th>$z_{br}$</th>
<th>$n_i$</th>
<th>$l_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kg/mol</td>
<td>#/chain</td>
<td>kg/mol</td>
<td>#/chain</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>PE-1</td>
<td>98</td>
<td>0.127</td>
<td>0.130</td>
<td>17</td>
<td>0.050</td>
<td>7.7</td>
</tr>
<tr>
<td>$\Sigma w_j X_j$</td>
<td>106</td>
<td>0.150</td>
<td>0.115</td>
<td>25</td>
<td>0.070</td>
<td>7.6</td>
</tr>
</tbody>
</table>

V.5.2 Quantification of Branching in LLDPE Fractions

Fig. 3 plots the TREF elution temperature against the number of SCBs per 1000 carbon atoms from NMR. A linear increase in SCB content with decreasing elution temperature is observed. Fig. 3 also plots the persistence length, $l_p$, from SANS versus the NMR SCB content. In a previous study, the relationship between $l_p$ and SCB content in equation (8) was obtained for ethyl short-chain branched polyethylene. In equation (8), $A$ represents the range of change in the value of $l_p$ with SCB content and $l_p^\infty = l_p^0 + A$, where $l_p^0 = 6.5$ Å for linear polyethylene with no short-chain branching. The SCB branch length is not expected to affect the maximum persistence length that can be obtained. In other words, the steric hindrance (that increases $l_p$) at maximum interference with chain motion remains approximately the same. Thus by fitting the data in Fig. 3 while keeping $A$ and $l_p^\infty$ constant, $\tau$ is determined to be $24.6 \pm 4.7$. $1/\tau$ is proportional to the rate at which $l_p$ increases with SCB content. The higher value of $\tau$ for butyl SCBs when compared to ethyl SCBs signifies a lesser effect of the number of SCBs on the persistence length. That is, a
higher SCB content is needed to increase persistence length for butyl SCBs compared to ethyl SCBs. Hence, each butyl branch has a smaller steric effect on persistence length compared to each ethyl branch. This observation is contrary to the results seen in some simulation studies\textsuperscript{33, 34} based on bead and spring models that predict a larger steric effect with increasing SCB branch length. In the case of polyethylene, this discrepancy with simulation results may arise because SCB branch length can affect the local structure of the polymer in ways other than just sterically. For instance, ethyl short-chain branches could additionally introduce a helicity in the local structure analogous to the methyl side group in polypropylene, thereby sharply increasing the persistence length at low levels of branching. However, polyethylene with butyl branches might maintain a planar zigzag structure which results in a slower increase in persistence length with SCB density. Further, the distribution of SCBs in the backbone (blockiness) and the end group effects due to length of the backbone can also influence the rate of increase in persistence length.

For the LLDPE fractions, it is seen that the persistence length increases progressively with decreasing elution temperature thereby implying a decrease in SCB content with elution temperature. This observation corroborates the mechanism of the TREF process which fractionates the sample based on the SCB content. Fig. 4a illustrates this trend in a plot of number of SCBs per 1000 carbon atoms, $n_{SCB}$ (right axis), against the weight-average molecular weight, $M_w$, of the fractions. Fig. 4a also plots the mole-fraction long-chain branch content, $\phi_{br}$ (left axis), against $M_w$. It is seen that the lower molecular weight fractions have extremely low amounts of LCBs (up to $\phi_{br} = 0.1$) with the higher molecular weight fractions displaying LCB
content of $\phi_{br} \sim 0.2$ to 0.3. PE-1 contains smaller amounts of these high molecular weight fractions (about 25% by weight) and displays a low $\phi_{br}$ of 0.127.

Ziegler-Natta Ti-based LLDPE resins are not expected to contain LCB, since polymerization from such catalyst systems does not produce vinyl unsaturation via $\beta$-hydrogen abstraction, which is necessary to produce LCB.\textsuperscript{35, 36} This vinyl re-incorporation mechanism is seen as the reason behind the formation of LCBs in other catalyst systems such as metallocenes.\textsuperscript{37} A different mechanism for introduction of long-chain branching in Ziegler-Natta systems has been reported by Reinking et al.\textsuperscript{35} Reinking et al. propose that LCBs may be introduced via C-H bond activation on the polymer backbone through $\sigma$-bond metathesis, followed by insertion of ethylene into the newly formed metal–carbon bond.\textsuperscript{35} The SANS method used here has been successful in quantifying low amounts of LCBs in polyethylene previously.\textsuperscript{13} The results reported in this article coupled with evidence reported previously\textsuperscript{35} may suggest that Ti-based Ziegler-Natta catalysts possibly lead to low amounts of long-chain branching in some LLDPE.

An alternative explanation for the presence of long-chain branching in the higher fractions of the LLDPE studied here may be a result of the change in molecular structure during processing of polyethylene. The LLDPE polymer used in this study was post-processed. It has been previously hypothesized\textsuperscript{7} that processing techniques such as extrusion, in the absence of air, introduce low levels of long-chain branching that result in unexpected rheological properties. Moreover, it is expected that LCBs are introduced preferentially in the higher molecular weight
chains of the resin. The results here support this conjecture. A pre-processed sample (straight from reactor) was not available for comparison for the LLDPE that was fractionated. But both pre-processed (powder) and post-processed (pellets) samples of a similar LLDPE (labeled LLDPE-2) were analyzed using the scaling approach. Fig. 4a plots the mole-fraction long-chain branch content, $\phi_{br}$, of LLDPE-2. It is seen that the LCB content of the sample from the reactor (powder) is lower than the LCB content of the post-processed (pellets) sample. This observation indicates that processing could introduce long-chain branching in polyethylene.
Figure 2. SANS data from Fraction 11 fit to the Unified Function in equation (4). Data shown above was acquired at NIST.
Figure 3. Persistence length, $l_p$, from SANS (left axis) and TREF elution temperature (right axis) versus the number of SCBs per 1000 Carbon atoms from NMR. The open triangle represents linear polyethylene with no SCBs with $l_p=6.5$ Å.
Figure 4a. Plot of mole-fraction LCB content, $\phi_{br}$, from equation (7) and number of SCBs per 1000 Carbon atoms, $n_{SCB}$, from NMR against the weight-average molecular weight, $M_w$, obtained from SANS.
Figure 4b. Plot of number of LCB sites per chain, $n_{br}$, from equation (6) and number of inner segments per chain, $n_i$, versus $M_w$. The filled data points represent the corresponding values obtained for PE-1 that was fractionated by TREF.
Fig. 4b plots the number of long-chain branch sites per chain, $n_{br}$, and number of inner segments, $n_i$, versus $M_w$ of the fractions. The method to obtain these quantities has been explained in detail previously.\textsuperscript{13} For the LLDPE fractions, very low $n_{br}$ and $n_i$ are observed for the lower molecular weight fractions and slightly higher values for the higher molecular weight fractions. The filled data points in Fig. 4b represent the corresponding values for PE-1. Since PE-1 has smaller amounts of the high molecular weight fractions, low values for $n_{br}$ and $n_i$ are observed. As tabulated in Table 1, the average long-chain branch length, $z_{br}$, is nearly 3 to 7 times higher for the higher fractions when compared to lower fractions.

V.6 Conclusions

A novel scaling model was applied to small-angle neutron scattering data for dilute solutions of linear low-density polyethylene fractions that were obtained from preparative temperature rising elution fractionation. This method was able to differentiate and quantify the short-chain branch content ($n_{SCB}$) and long-chain branch content ($\phi_{br}$) simultaneously for the fractions. Consequently, the branch length distribution in the LLDPE sample was investigated. In addition, the effect of the short-chain branch length on the structure of polyethylene was determined. While the results confirm that TREF separates the fraction in a polymer based on the SCB content, it also shows evidence of sparse amounts of long-chain branching that are usually undetected by traditional characterization techniques. For Ziegler-Natta systems, the results reported here are consistent with both a mechanism based on $\sigma$-bond metathesis for producing LCBs\textsuperscript{35} and processing as a source of LCBs in polyethylene.\textsuperscript{7} The number of LCB sites per chain ($n_{br}$), number of inner segments per chain ($n_i$) and average LCB length ($z_{br}$) were reported for the
LLDPE fractions, providing further insight into the architectural distribution of these features in a commercial LLDPE resin.

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V.7 References


CHAPTER VI

Conclusions and Future Work
VI.1 Conclusions

A novel scaling approach to quantify the topology of complex macromolecular structures has been presented in this dissertation.\textsuperscript{1-5} Specifically the scaling approach is applied to quantify the branch content in polyethylene. The scaling approach when applied to small-angle neutron scattering data from very dilute solutions of polyethylene in a good solvent is able to provide a comprehensive quantification of branching in polyethylene. Using this approach new quantities such as mole fraction long-chain branch content, $\phi_{br}$, average number of long-chain branch sites per chain, $n_{br}$, average number of inner segments per chain, $n_i$, and average long-chain branch length, $z_{br}$, can be estimated for branched polyethylene. Additionally the short-chain branch content in polyethylene can also be estimated based on the measurement of the persistence length, $l_p$. Such detailed description of the architectural makeup of polyethylene can result in improved understanding of its structure-property relationships.

Polyethylene is not only one of the most important commercial polymers with many applications, it is also available in a number of different architectures with varying long-chain and short-chain branch content. The versatility of the polyethylene made it an ideal choice to develop and validate the new scaling/SANS approach. In this dissertation, the approach is applied to a variety of model and commercial polyethylene resins.

Chapter II\textsuperscript{3} uses the scaling/SANS approach to investigate the effect of short-chain branching on the persistence length, $l_p$, of polyethylene. Short-chain branching (typically in the
form of ethyl or butyl branches) affects the local structure of polyethylene by causing steric hindrance. The steric effects lead to increase in the persistence length of polyethylene that can be measured from SANS. The values obtained, ranged from $6.5 \pm 0.8$ Å (for linear polyethylene NIST SRM 1484) to $9.0 \pm 0.60$ Å for polyethylene with 12.1 branches per 1000 carbon atoms. A relationship was developed to relate the short-chain branch content of polyethylene with ethyl SCBs to the persistence length of polyethylene. A maximum enhancement of persistence length to $9.1$ Å for fully branched PE is also observed. In chapter V, this approach was extended to study the effect of short-chain branch length on the aforementioned relationship.

In Chapter III, the scaling/SANS approach is applied to quantify the branch content in commercial model high-density polyethylene resins. The new quantities measured in this approach such as $z_{br}$ and $n_i$ are related to rheological properties like zero-shear rate viscosity enhancement of polyethylene. Such correlations provide enhanced understanding of the structure-property relationships in polyethylene. Particularly, with respect to hyperbranching which is quantified in terms of the average number of inner segments per chain, $n_i$, results in chapter III along with results shown in appendix II provides new insights in to the relationship between viscosity enhancement due to branching and the hyperbranch content in polyethylene.

Chapter IV further validates the new approach by applying the scaling/SANS method to quantify the branch content in model 3-arm star polyethylene resins. The measurements of $\phi_{br}$ and $z_{br}$ made via the approach presented in this dissertation shows good correlation with the
calculated averages for these model 3-arm star resins. In appendix III, the approach is extended to quantify the branch content in blends of branched polyethylene with linear counterparts.

Chapter V describes how the scaling/SANS approach can be used to study the branch length distribution in commercial polydisperse polyethylene. Fractions of polyethylene were obtained via temperature rising elution fractionation (TREF) for this study. Results from this analysis give further insights into the effects of processing and catalyst systems on the structure of polyethylene. Additionally, this study corroborates the fact that the quantities measured from SANS are in fact weight-averaged quantities.

The scaling model described in this dissertation has been applied to quantify the structure of such as ceramic aggregates, cyclic polymers and to quantify the degree of folding in proteins and RNA. On-going and future applications of the method developed in this dissertation are summarized in the following section.
VI.2 Future Work

The work presented in the dissertation has opened many avenues to applying the scaling approach to other complex materials. The scaling method can be combined with suitable small-angle scattering techniques to investigate the structure of other ramified structures. Some possible applications are discussed here.

Graphene nano-sheets have shown tremendous potential in applications such as integrated circuits and solar cells.\textsuperscript{8-10} The properties that make these materials attractive are directly related to their microstructure. The scaling approach can be applied to quantify the complex structure of graphene and relate the structure to the physical and electrical properties of the material. Currently, the application of graphene in solar cells is being investigated at the University of Cincinnati. Additionally, the scaling approach is being combined with small-angle X-ray scattering (SAXS) to investigate the aggregate structure of silicon and titania for use in printed electronics.\textsuperscript{11} The enhanced quantification available from the scaling method can be used to better understand the structure-property relationships in these materials. For example, the resistivity of a single conduction pathway might be calculated from $\rho/d_p^2$, where $\rho$ is the minimum path estimated from the scaling approach and $d_p$ is the Sauter mean diameter of a primary particle measured in SANS. The overall conductivity of the aggregate depends on the connectivity of parallel conduction pathways through the aggregate.\textsuperscript{11}
The scaling model described in this dissertation can also be applied to star polymers that display fractal behavior with uniform chain density. This is expected in star polymers with functionality, \( f \leq 8 \) and moderate molecular weight. For star polymers with \( f > 8 \), the Daoud and Cotton model\textsuperscript{12} predicts a morphology with a collapsed core and the chains (arms) confined to a shells of variable chain scaling. In a small-angle scattering profile, the collapsed core will display Porod behavior. The scaling/SANS approach can be used to determine the functionality that causes the transition from a mass-fractal scaling to a collapsed morphology\textsuperscript{13}.

One of the main outcomes of the work presented here has been the formation of the Center for Macromolecular Topology. This a multi-organization effort that will be based at the University of Cincinnati with partners including various companies like LyondellBasell, Procter&Gamble, DuPont, Dow Chemicals, Exxon-Mobil, SABIC, Celanese etc. as well as the National Science Foundation, Oak Ridge National Laboratory, National Insitute of Standards and Technology and the University of Michigan. The aim of the centre is to provide a resource that makes small-angle scattering techniques like SANS more accessible to a broad group of scientists and provide new oppurtunities for the application of the scaling method in investigating new complex materials.
References


APPENDIX I

Accounting for Polydispersity in Scaling/SANS Approach
Accounting for Polydispersity in Scaling/SANS Approach

In commercial polymers like polyethylene, polydispersity plays a significant role in accurately quantifying branching in the structure. For instance, the effects of long-chain branching and the effects of polydispersity on rheological properties are similar, thereby making it difficult to distinguish them.\textsuperscript{1-4} In the scaling/SANS approach the effect of polydispersity is observed in the low $q$ range of the SANS data. In order to account for the polydispersity in a resin, a polydispersity factor, $C_p$, is introduced in the fitting routine of the SANS data.\textsuperscript{5-8}

Description of $C_p$

SANS data is fit using the Unified Function\textsuperscript{5-7, 9-15} as show in Figure 1. The Unified Function is given by:

\begin{equation}
I(q) = \left\{ G_2 e^{-\left(\frac{q^2 R_g^2}{2}\right)\frac{1}{3}} + B_2 e^{-\left(\frac{q^2 R_g^2}{18}\right)\frac{1}{3}\left(q_2^*\right)^3} \right\} + \left\{ G_1 e^{-\left(\frac{q^2 R_g^2}{9}\right)\frac{1}{3}} + B_1 \left(q_1^*\right)^{-1} \right\}
\end{equation}

where $q_i^* = \left[ \frac{q}{\text{erf}(qkR_g^i / \sqrt{6})^{3/2}} \right]$ and $k\approx1.06$

In the above equation, the terms in the first bracket with subscript “2” represent the good solvent scaling regime with mass-fractal dimension $d_f^2 \geq 5/3$ (fits the low and medium $q$ range of SANS data) and the second bracket with subscript “1” represent the rod-like persistent scaling regime (high $q$-range of SANS data).
Figure 1. SANS data from short-chain branched PE. The slopes -5/3 and -1 indicate scaling at two separate structural regimes. Unified Fit is according to Equation (1). Data shown above was obtained at NIST.

The power-law prefactor $B_2$ for the mass-fractal regime (low $q$- regime) is modified to account for polydispersity and is given by;

$$B_2 = \frac{C_{p} d_{\text{min}} G_2}{R_{g}^{d_{f}/2}} \Gamma(d_{f}/2)$$

(2)

where $\Gamma$ is the gamma function. $C_{p}$ is obtained from fitting the SANS data (the parameter is floated during the fitting routine) using the modified expression for $B_2$ in equation (2).\textsuperscript{8}
\( C_p \) is a scattering polydispersity factor given by: \(^8\)

\[
C_p = \frac{z_1}{z_2} \left( \frac{z_{2+d_2/2}}{z_2} \right)^{d_{f2}/2}
\]

(3)

where \( z_i \) is the \( i^{th} \) moment of the molecular weight distribution. Considering the trivial cases of either a linear polymer melt or a linear polymer in theta solvent, \( C_p \) equals \( M_\ell/M_w \) when \( d_{f2} = 2 \). Since the scaling/SANS approach is routinely used to analyze branched PE resins in dilute good solvent (\( d_{f2} > 5/3 \)), \( C_p \) obtained varies from the trivial form.

In order to obtain a fair estimation of \( C_p \) expected from the fitting routine for a polydisperse resin, the plot in figure 2 is used as reference. The correlation in figure 2 was generated based on the data collected for a variety of PE resins wherein \( C_p \) obtained from SANS is compared to \( M_\ell/M_w \) ratio that is obtained from GPC. Before fitting the SANS data for the first time using the Unified Function, reasonable predictions are made for the various parameters that are used to fit the data. This results in rapid convergence to repeatable results that are generated from the fitting routine. For \( C_p \), the correlation in figure 2 is used to make a reasonable initial estimate.
Figure 2. Plot of $C_p$ from SANS vs. $M_z/M_w$ from GPC

\[ C_p = 0.73 + 0.27 \frac{M_z}{M_w} \]
References


APPENDIX II

Effect of Hyperbranching on Zero-Shear Rate Viscosity Enhancement
Effect of Hyperbranching on Zero-Shear Rate Viscosity Enhancement

The viscosity enhancement in branched polyethylene can be attributed to hyperbranching in the polymer chains.\textsuperscript{1, 2} Hyperbranching is quantified in terms of the average number of inner segments per chain, $n_i$, and is obtained from the scaling/SANS approach by

$$n_i = n_{br} - n_{br,p} \quad (1)$$

where $n_{br}$ is the average number of long-chain branches per chain and $n_{br,p}$ is the average number of long-chain branches in the minimum path.

In Chapter III, the effect of hyperbranched (branch-on-branch) segments on the zero-shear viscosity was discussed as shown in Figure 1. Essentially, for low levels of hyperbranching in the high-density polyethylene resins, a linear increase in viscosity enhancement with increasing number of inner segments was observed. Subsequently, the scaling/SANS approach was carried out on resins with higher long-chain branch content and higher hyperbranch content. Figure 2 shows a composite plot of the change in zero-shear rate viscosity enhancement with hyperbranch content for the Dow HDB HDPE series, and certain other HDPE and LDPE resins with varying long-chain branch and hyperbranch content. While the zero-shear rate viscosity enhancement increased linearly for low levels of hyperbranching, a decrease in the viscosity enhancement due to branching was observed for high levels of long-chain branching.
Figure 1. Linear plot of zero-shear rate viscosity enhancement w.r.t linear polyethylene of same $M_w$ against number of inner segments per chain, $n_i$, for the HDB samples. The error in $n_i$ for HDB-1 is smaller than the point size.$^3$
**Figure 2.** Zero-shear rate viscosity enhancement for various branched polyethylene against number of inner segments per chain, $n_i$. 
Such a behavior has been observed before, for instance in the case of branched polypropylene.\textsuperscript{4} Figure 3 shows the change in the zero-shear rate viscosity enhancement with increasing irradiation dose. Irradiation is a common technique to introduce long-chain branching in polypropylene and a higher irradiation dose corresponds to higher levels of long-chain branching and hyperbranching. Similar to the behavior that is seen in figure 2 for polyethylene, polypropylene shows a sharp increase in the zero-shear rate viscosity enhancement at low levels of branching and decreases with increased levels of branching (higher irradiation dose).

Based on the current study, the rationale for this behavior can be explained as below. Hyperbranched segments or inner segments differ from the other segments in a polymer chain in that they are connected at both ends (in other words, they do not have a free end). This renders the segment immovable in terms of flow. When low numbers of these segments are present in a polymer melt, it hinders the reptation of the chains to escape entanglements. This contributes to a sharp increase in the zero-shear rate viscosity. The decrease in the viscosity enhancement with increased levels of hyperbranching can possibly occur due to the onset of melt fracture.\textsuperscript{5} The current study represents the first time that such a behavior can be correlated to a quantifiable feature of the structure.
Figure 3. Zero-shear rate viscosity enhancement for branched polypropylene vs. irradiation dose.
References


APPENDIX III

Quantification of Branching in Polyethylene Blends
Quantification of Branching in Polyethylene Blends

Commercial polyethylenes are frequently blended to attain certain desired physical and processing properties. The scaling/SANS approach can be used to estimate branch content in polyethylene blends. In this appendix, results obtained from quantification of branching in blends of model branched polyethylene resins with model linear polyethylene resins are presented.\textsuperscript{1, 2}

Table 1 lists the homopolymers\textsuperscript{1, 2} used to make the blends. The weight-average molecular weight, $M_w$, and polydispersity index, PDI, measured from SEC-MALLS are listed along with quantities measured from scaling/SANS approach\textsuperscript{3-5} for these resins: weight-average molecular weight, $M_w$, mole-fraction long chain branch content, $\phi_{br}$, and weight-average long-chain branch length, $z_{br}$. A description of the various homopolymers is given below.

a. PELM 110 – Model linear polyethylene
b. PES(53)\textsubscript{3} – MS2, Model symmetric 3-arm star polyethylene
c. PEC(57)(22)\textsubscript{15} – COM18, Model comb shaped polyethylene
d. PEPP(12)\textsubscript{5}(80)(12)\textsubscript{5} – PP5-6, Model pom-pom shaped polyethylene
e. PEH(10)\textsubscript{2}(95)(10)\textsubscript{2} – EH4, Model H-shaped polyethylene
Table 1: Homopolymers used to make blends of polyethylene

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (kg/mol)$^a$</th>
<th>PDI</th>
<th>$M_w$ (kg/mol)$^b$</th>
<th>$\phi_{br}$</th>
<th>$z_{br}$ (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PELM110</td>
<td>110</td>
<td>1.13</td>
<td>115±8</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PES(53)$_3$</td>
<td>139</td>
<td>1.12</td>
<td>132±7</td>
<td>0.34±0.02</td>
<td>49±7</td>
</tr>
<tr>
<td>PEC(57)(22)$_{15}$</td>
<td>NA</td>
<td>NA</td>
<td>400±21</td>
<td>0.85±0.04</td>
<td>43±6</td>
</tr>
<tr>
<td>PEPP(12)$_5$(80)(12)$_5$</td>
<td>195</td>
<td>1.07</td>
<td>184±10</td>
<td>0.79±0.03</td>
<td>19±4</td>
</tr>
<tr>
<td>PEH(10)$_2$(95)(10)$_2$</td>
<td>162</td>
<td>1.04</td>
<td>137±7</td>
<td>0.55±0.02</td>
<td>74±9</td>
</tr>
</tbody>
</table>

$^a$measured by SEC-MALLS$^1, 2$

$^b$measured by SANS.

Table 2 lists the blends that were analyzed along with the quantities measured from the scaling/SANS approach: weight-average molecular weight, $M_w$, mole-fraction long chain branch content, $\phi_{br}$, and weight-average long-chain branch length, $z_{br}$. Four different compositions were prepared for each blend. The percentages are given by weight. Compositions of the blends are listed below.

**Blend 1**

1a. 50% PELM110, 50% MS2
1b. 75% PELM110, 25% MS2
1c. 90% PELM110, 10% MS2
1d. 98% PELM110, 2% MS2
Blend 2
2a. 50% PELM110, 50% COM18
2b. 75% PELM110, 25% COM18
2c. 90% PELM110, 10% COM18
2d. 98% PELM110, 2% COM18

Blend 3
3a. 50% PELM110, 50% PP5-6
3b. 75% PELM110, 25% PP5-6
3c. 90% PELM110, 10% PP5-6
3d. 98% PELM110, 2% PP5-6

Blend 4
4a. 50% PELM110, 50% EH4
4b. 75% PELM110, 25% EH4
4c. 90% PELM110, 10% EH4
4d. 98% PELM110, 2% EH4
Table 2: Quantification of branch content for blends of polyethylene.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (kg/mol)</th>
<th>$\phi_{br}$</th>
<th>$z_{br}$ (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blend 1a</td>
<td>128±8</td>
<td>0.22±0.01</td>
<td>51±7</td>
</tr>
<tr>
<td>Blend 1b</td>
<td>129±7</td>
<td>0.12±0.01</td>
<td>51±7</td>
</tr>
<tr>
<td>Blend 1c</td>
<td>117±21</td>
<td>0.07±0.01</td>
<td>56±6</td>
</tr>
<tr>
<td>Blend 1d</td>
<td>113±10</td>
<td>0.01±0.01</td>
<td>54±8</td>
</tr>
<tr>
<td>Blend 2a</td>
<td>287±12</td>
<td>0.67±0.03</td>
<td>46±6</td>
</tr>
<tr>
<td>Blend 2b</td>
<td>210±21</td>
<td>0.51±0.02</td>
<td>38±6</td>
</tr>
<tr>
<td>Blend 2c</td>
<td>156±23</td>
<td>0.20±0.01</td>
<td>39±6</td>
</tr>
<tr>
<td>Blend 2d</td>
<td>137±12</td>
<td>0.08±0.01</td>
<td>56±8</td>
</tr>
<tr>
<td>Blend 3a</td>
<td>148±1</td>
<td>0.53±0.03</td>
<td>24±4</td>
</tr>
<tr>
<td>Blend 3b</td>
<td>140±1</td>
<td>0.38±0.02</td>
<td>20±3</td>
</tr>
<tr>
<td>Blend 3c</td>
<td>128±2</td>
<td>0.18±0.02</td>
<td>27±4</td>
</tr>
<tr>
<td>Blend 3d</td>
<td>124±2</td>
<td>0.04±0.01</td>
<td>28±4</td>
</tr>
<tr>
<td>Blend 4a</td>
<td>146±2</td>
<td>0.36±0.02</td>
<td>82±9</td>
</tr>
<tr>
<td>Blend 4b</td>
<td>135±3</td>
<td>0.21±0.01</td>
<td>65±8</td>
</tr>
<tr>
<td>Blend 4c</td>
<td>125±4</td>
<td>0.05±0.01</td>
<td>67±8</td>
</tr>
<tr>
<td>Blend 4d</td>
<td>115±5</td>
<td>0.04±0.01</td>
<td>79±8</td>
</tr>
</tbody>
</table>

Figure 1 plots the molecular weight of blends measured from scaling/SANS approach versus the weight-average molecular weight measured from SEC-MALLS. The near one-to-one correlation confirms that molecular weight measured from SANS is in fact a weight-average quantity. Figure 2 plots the mole-fraction branch content, $\phi_{br}$, versus the weight-average composition of the blend, $\phi_{2nd}$, with respect to the branched component which is given by
\[ \phi_{2nd} = \frac{n_2 M_2^2}{\sum n_i M_i^2} \]  

where \( n_2 \) and \( M_2 \) is the weight fraction and weight-average molecular weight of the branched component respectively. \( n_i \) and \( M_i \) is the weight fraction and weight-average molecular weight of the linear component or the branched component of the blend respectively. A linear trend is observed for all the blends in figure 2 suggesting that the mole-fraction branch content of the blends linearly with the weight-average blend composition of the branched component. Hence, if the blend composition is available, it is possible to determine the branch content of the blend when the branch content of the individual homopolymers is known and vice-versa.

A key distinction in the average branch length of a branched polymer, \( z_{br} \), when compared to the mole-fraction branch content, \( \phi_{br} \), is that \( z_{br} \) does not change with blending of a branched polymer with a linear polymer. In figure 3, the weight-average long-chain branch length, \( z_{br} \), measured from the scaling/SANS approach is plotted against the blend composition, \( \phi_{2nd} \). The analysis for the various blends indicates that \( z_{br} \) measured from SANS remains reasonably unchanged by blending a branched polymer with a linear polymer.
Figure 1. Plot of weight-average molecular weight, $M_w$, of the blends and PELM110 (linear polyethylene) obtained from SANS versus the weight-average molecular weight, $M_w$, obtained from SEC-MALLS.
Figure 2. Plot of mole-fraction long-chain branch content, $\phi_{br}$, for the blends calculated from SANS versus the weight-average blend composition of the branched component.
Figure 3. Plot of weight-average long-chain branch length, $z_{br}$, for the blends calculated from SANS versus the weight-average blend composition of the branched component.
References


APPENDIX IV

Illustrating Branched Polyethylene from the Scaling/SANS Approach
Illustrating Branched Polyethylene from the Scaling/SANS Approach

One of the goals in developing the scaling/SANS approach to quantify branched polymers was to make the approach comprehensive enough to illustrate the polymer chains in a melt. Such an illustration can provide catalyst chemists with an enhanced picture of the polymer that can help them better understand the effects of current catalyst systems and produce new catalyst systems to design different polyethylene structures. In this appendix, a step-by-step description is provided to facilitate such an illustration. Additionally, the illustration is used to distinguish the effects of various catalyst systems on the structure of high-density polyethylene resins. The following quantities are available from the scaling/SANS approach to describe branched polyethylene.1-3

i. $n_{br}$ – Average number of LCBs per chain

ii. $n_i$ – Average number of hyperbranch segments per chain

iii. $\phi_{br}$ – Mole fraction LCB content

iv. $M_w$ – Weight-average molecular weight

v. $z_{br}$ – Weight-average LCB length

vi. Ratio $M_w/z_{br}$

The polydispersity index ($M_w/M_n$, $PDI$), is also available from standard GPC measurements.

By definition:

a. $z_{br}$ is calculated from the chains that have LCBs. In other words, $z_{br}$ is unaffected by presence of linear chains in a polydisperse resin. This fact is used to accommodate for polydispersity in the resin.
b. $\phi_{br}$ (unlike $z_{br}$) is calculated for all chains. For instance, a pure symmetric 3-arm star resin will have a $\phi_{br}$ of 0.33. Whereas a mixture of linear and 3-arm stars will have a $\phi_{br}$ lower than 0.33. The measured value of $\phi_{br}$ is linear with the weight average composition of the branched component.

List of assumptions:

a. The picture provided is a low resolution representation (10 chains) of the actual resin.

b. The LCB lengths are assumed to be monodisperse.

c. The location of an LCB in a particular chain is assumed to be random. Sufficient information to predict the exact location of the LCB in each chain is unavailable. For instance, in a polydisperse mixture, it is not possible to differentiate between symmetric and asymmetric 3-arm stars.

c. A block distribution (mono-modal) of molecular weights is assumed.

**Illustration of the polyethylene structure**

1. Consider a population of 10 chains

2. The weight-average molecular weight and polydispersity index give an estimate of the size and dispersity of chains present in the resin. This allows for creating a template for the resin under consideration.
Table 1: Quantification of branching in three polyethylene resins obtained from different catalyst systems. The values listed are average for each type of resin

<table>
<thead>
<tr>
<th></th>
<th>Resin 1</th>
<th>Resin 2</th>
<th>Resin 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDI</td>
<td>30</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>$M_w$ (g/mol)</td>
<td>260,000</td>
<td>195,000</td>
<td>365,000</td>
</tr>
<tr>
<td>$n_{br}$</td>
<td>0.9</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>$n_i$</td>
<td>0.1</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>$\phi_{br}$</td>
<td>0.36</td>
<td>0.23</td>
<td>0.45</td>
</tr>
<tr>
<td>$z_{br}$ (g/mol)</td>
<td>15,000</td>
<td>20,500</td>
<td>16,000</td>
</tr>
<tr>
<td>Ratio $M_w/z_{br}$</td>
<td>17</td>
<td>10</td>
<td>23</td>
</tr>
</tbody>
</table>

3. For a population of 10 chains, considering the PDI, it is observed that the high molecular weight chain is about 30, 9 and 7 times the low molecular weight chain for the Resin 1, Resin 2 and Resin 3 respectively. Using this information along with the molecular weight, the following template (Figure 1) can be drawn (assuming monomodal distribution of molecular weight)

Figure 1. Template for the 3 resins under consideration.
4. The next step is to introduce the LCBs in the picture. The following information is utilized.

a. $n_{br}$ gives the average number of branches per chain. $n_i$ gives the average number of hyperbranch segments per chain.

b. A value of $n_{br} = 0.9$ (as in the case of Resin 1 in Table 1) should be read as 9 LCBs in 10 chains. Similar description is used for $n_i$ as well.

c. $z_{br}$ gives the average long chain branch length. $\phi_{br}$ gives the fraction of the polymer present in branches.

5. In a population of 10 chains:

a. For Resin 1, there are 9 LCBs and 1 hyperbranch segment.

b. For Resin 2, there are 4 LCBs and 1 hyperbranch segment.

c. For Resin 3, there are 12 LCBs and 4 hyperbranch segments.

d. The ratio of $M_w$ over $z_{br}$, (17, 10 and 23 times $z_{br}$ in the case of Resin 1, Resin 2 and Resin 3 respectively) along with $\phi_{br}$ leads to the prediction that the LCBs are present in the low molecular weight chains. (Since LCB in the high molecular weight chains will reduce the value of $\phi_{br}$ to lower than what is measured from SANS)

6. The final picture for the resins (Figure 2) is obtained by updating the template in Figure 1 based on steps 4 and 5.
Comparing HDPE resins from different catalyst systems

Commercial high-density polyethylene (HDPE) is produced by employing a variety of catalyst systems such as Zeigler-Natta catalysts, Metallocene catalysts and Chromium oxide catalysts.\textsuperscript{4} Each of these catalysts has different effects on the resulting structure of the HDPE. The quantification of the branching from the scaling/SANS approach can be useful in distinguishing the subtle differences to the structure.\textsuperscript{1-3} Figure 3 compares the molecular weight and weight-average branch length for the various resins. A low-density polyethylene (LDPE) resin produced using the free radical process is also shown for comparative purposes. Figure 4 compares the mole-fraction long-chain branch content, $\phi_{br}$, for the various HDPE resins from...
different catalyst systems and the free radical LDPE resin. The metallocene HDPE has the lowest $\phi_{br}$ followed by the chrome resin, Ziegler resins and LDPE. Figure 5 compares the hyperbranch content (branch-on-branch) in terms of the average number of inner segments per chain, $n_i$, for the various resins. The metallocene HDPE has the lowest hyperbranch content followed by the Ziegler resins, chrome resin and LDPE.

Using the information from figures 3, 4 and 5 and combining it with the average number of long-chain branches per chain, $n_{br}$, obtained from the scaling/SANS approach, an illustration can be provided as shown in figure 6 that compares the effect of the various catalyst systems on the structure of high-density polyethylene. The metallocene HDPE displays the lowest levels of long-chain branching (about 1 LCB per 10 chains) and hyperbranching. The Ziegler-Natta resins have higher levels of LCB (about 4 LCBs per 10 chains) compared to metallocene resins but similar low levels of hyperbranching. The HDPE resin obtained from chromium oxide catalyst shows the highest levels of LCB and hyperbranching among the HDPE’s. The LDPE resin has the highest levels of LCB and hyperbranching among all the resins compared which is a direct result of the free radical process used to produce LDPE. Such comprehensive quantification and depiction of branching in polyethylene can provide a better description of how various catalyst systems affect the resulting branched structures.
Figure 3. Comparing the molecular weights and weigh-average branch length obtained from the scaling/SANS approach for HDPEs and LDPE.
Figure 4. Comparing mole-fraction long-chain branch content, $\phi_{br}$, obtained from the scaling/SANS approach for HDPEs and LDPE.
Figure 5. Comparing average number of inner segments per chain, $n_i$, obtained from the scaling/SANS approach for HDPEs and LDPE.
Figure 6. Comparing average number of long-chain branches per chain, $n_{br}$, obtained from the scaling/SANS approach for HDPEs and LDPE.
References


