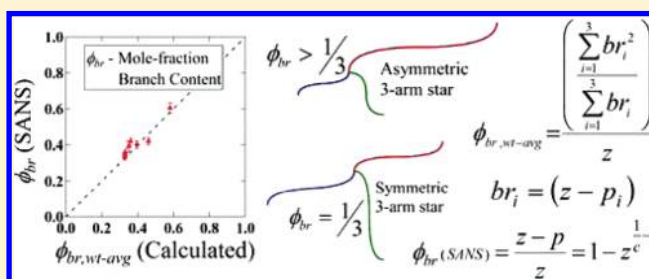


Quantification of Branching in Model Three-Arm Star Polyethylene

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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 analogues 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.



■ 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 are 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 incomplete 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 branching⁹ 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.^{13–15} 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

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possible to synthesize polyethylene directly by this technique, it is possible to synthesize model polybutadiene that can be hydrogenated to eliminate unsaturation and form analogues of polyethylene.^{1,16} 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.¹⁴ Long-chain branched polybutadiene can be prepared using chlorosilane condensation chemistry.^{1,16,17} Hadjichristidis et al. have synthesized¹ a variety of model branched polyethylene analogues by hydrogenating branched polybutadienes. These include polyethylene with 3-arm star, comb, H, and pom-pom as well as dendritic¹⁸ architectures. In this article, the aforementioned scaling approach^{4,5,8} is applied to quantify the structure of model 3-arm star polyethylene synthesized by Hadjichristidis et al.¹ The versatility of the scaling approach is highlighted here by presenting the detailed quantification of such model branched polyethylene resins.

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 or Kuhn length $l_k \approx 2l_p$.¹⁹ [Additionally, a dynamic size close to l_p called the packing length³ can be defined which is not discussed here.] 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_{\min} . The tortuosity in the polyethylene chain is described by p and d_{\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

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

A scaling relationship between z , p and s can then be derived as^{5,8}

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

From eqs 1 and 2, a simple relationship is obtained, $d_f = cd_{\min}$, 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 $d_{\min} = 1$.

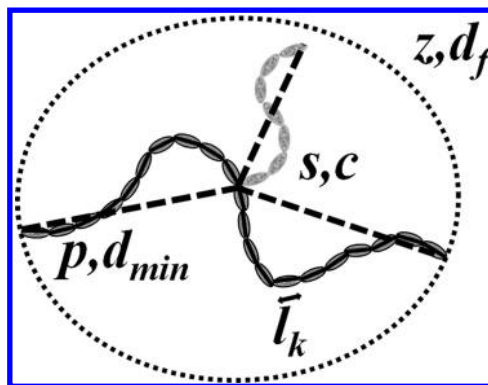


Figure 1. Schematic of a 3-arm star polymer in the scaling model. Each Kuhn step is represented by a bead. The polymer of mass-fractal dimension d_f is composed of z Kuhn steps of size l_k . The dark beads represent a minimum path p of dimension d_{\min} , composed of 2 arms. The lighter Kuhn steps depict 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 nonoverlapping extended conformation in order to distinguish the arms.

d_{\min} increases with tortuosity, c increases with increased connectivity. Thus, for linear polyethylene in a good solvent, $d_f = d_{\min} \approx 5/3$ and $c = 1$. For branched polyethylene in a good solvent, $d_f > d_{\min}$, $1 < c \leq d_f$, and $1 \leq d_{\min} \leq 5/3$.

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, ϕ_{br} , is obtained by,

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

The calculation of branch fraction for symmetric stars is trivial and can be calculated by,⁸ $\phi_{br} = (f - 2)/f$, where f is the functionality of the symmetric star. For asymmetric stars, three 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,

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

The Unified Function^{5,9,20,21} along with the scaling model⁸ 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_g^2 , G_2 , B_2 , G_1 , B_1 , and d_f .

$$I(q) = \{G_2 e^{-(q^2 R_g^2)/3} + B_2 e^{-(q^2 R_g^2)/3} (q_2^*)^{-d_{f2}}\} + \{G_1 e^{-(q^2 R_g^2)/3} + B_1 (q_1^*)^{-1}\} \quad (4)$$

where $q_i^* = [q / \{\text{erf}(qkR_g/\sqrt{6})\}^3]$ 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

Table 1. SANS Characterization of Model 3-Arm Star Polyethylene Resins

sample	M_w (kg/mol) ^a	PDI (M_w/M_n) ^a	M_w (kg/mol) ^b	ϕ_{br}	n_{br}	z_{br} (kg/mol)	n_i	ϕ_{si}
PES(50) ₂ (5)	130	1.03	135 ± 10	0.42 ± 0.02	1.21 ± 0.05	47 ± 5	0.23 ± 0.09	0.033 ± 0.005
PES(50) ₂ (15)	138	1.04	135 ± 8	0.40 ± 0.02	0.93 ± 0.04	54 ± 5	0.22 ± 0.08	0.026 ± 0.005
PES(50) ₂ (25)	131	1.06	134 ± 9	0.42 ± 0.02	0.97 ± 0.04	49 ± 5	0.26 ± 0.08	0.027 ± 0.005
PES(43) ₃	133	1.13	135 ± 9	0.34 ± 0.01	0.76 ± 0.03	44 ± 4	0.10 ± 0.05	0.026 ± 0.006
PES(15) ₂ (85)	129	1.17	128 ± 13	0.61 ± 0.03	1.88 ± 0.07	66 ± 6	1.00 ± 0.12	0.034 ± 0.005
PES(40) ₂ (60)	125	1.08	137 ± 8	0.39 ± 0.03	0.87 ± 0.06	59 ± 7	0.20 ± 0.10	0.024 ± 0.004
PES(27) ₃	82	1.04	103 ± 5	0.36 ± 0.02	0.90 ± 0.06	33 ± 4	0.10 ± 0.08	0.032 ± 0.005
PES(53) ₃	139	1.12	132 ± 7	0.34 ± 0.02	0.81 ± 0.05	49 ± 6	0.08 ± 0.06	0.025 ± 0.005
PES(48) ₃	138	1.21	146 ± 7	0.35 ± 0.01	0.80 ± 0.06	51 ± 4	0.11 ± 0.08	0.024 ± 0.004

^aMeasured by SEC–MALLS. ^bMeasured by SANS.

dimension, d_{min} , is calculated from these parameters and is given by^{5,8}

$$d_{min} = \frac{B_2 R_{g,2}^{d_f}}{C_p \Gamma\left(\frac{d_f}{2}\right) G_2} \quad (5)$$

where C_p is the polydispersity factor^{5,9,22} and Γ 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_f/d_{min} as described in the scaling model. From the topological parameters obtained, an expression is derived⁵ for the weight-average number of branch sites per chain, n_{br} , which is given by⁵

$$n_{br} = \left(\frac{z^{(5/2d_f - 3/2c) + (1 - 1/c)} - 1}{2} \right) \quad (6)$$

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

$$z_{br} = \frac{z \phi_{br} M_{Kuhn}}{n_{br,p}} \quad (7)$$

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/mol 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.

MATERIALS AND METHODS

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_2B) 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 analogues 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

°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 h prior to the measurements to ensure complete dissolution of the polymer. The polymer solution was stirred by means of micromagnetic stir bars to homogenize the solution prior to the measurement. One wt % solutions were used which is well below the overlap concentration²⁴ for all fractions. SANS experiments were carried out at NG-7 SANS²⁵ 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 h per sample.

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, ϕ_{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 ref 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, ϕ_{si} , which is described later in this article. The errors reported were propagated from the data.

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.²⁷ 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, ϕ_{br} , from eq 3, obtained from SANS against $\phi_{br,wt-avg}$ obtained from eq 3a. In a previous study⁶ 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-

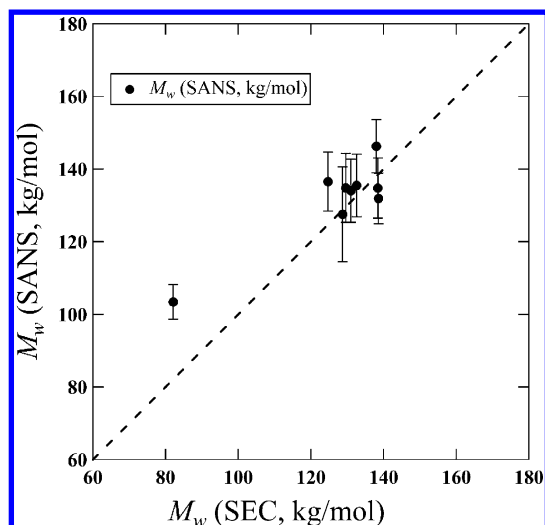


Figure 2. Plot of weight-average molar mass, M_w , obtained from SANS and weight-average molar mass, M_w , obtained from SEC-MALLS for 3-arm star polyethylenes.

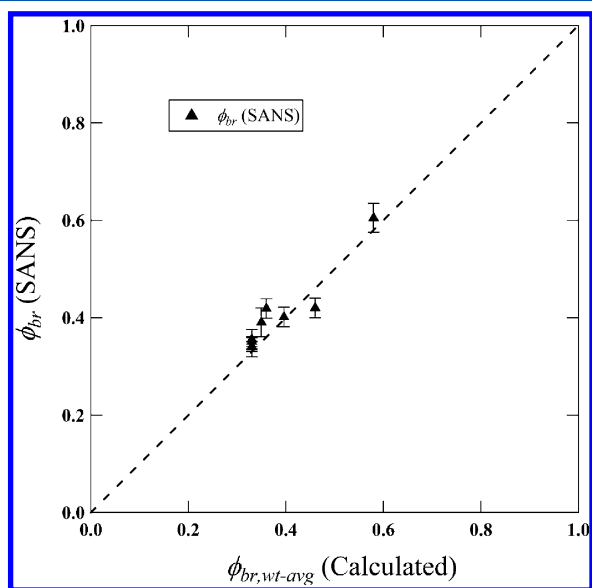


Figure 3. Plot of mole-fraction branch content, ϕ_{br} , from eq 3, obtained from SANS versus the calculated weight-average branch content, $\phi_{br,wt-avg}$, from eq 3a for 3-arm star polyethylenes.

average values calculated by summing the contribution from individual fractions. In the current study, the good correlation between ϕ_{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.

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

$$z_{br,wt-avg} = \frac{\sum_{i=1}^3 (arm)_i^2}{\sum_{i=1}^3 (arm)_i} \quad (8)$$

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

Table 2. Arm Lengths for 3-Arm Star Polyethylenes

sample	arm 1 (kg/mol)	arm 2 (kg/mol)	arm 3 (kg/mol)	$z_{br,wt-avg}$ (kg/mol)
PES(50) ₂ (5)	52	52	5.2	49.8
PES(50) ₂ (15)	52	52	15.5	47.3
PES(50) ₂ (25)	52	52	26	46.8
PES(43) ₃	44.5	44.5	44.5	44.5
PES(15) ₂ (85)	15.5	15.5	88.5	69.6
PES(40) ₂ (60)	42	42	62	50.5
PES(27) ₃	28	28	28	28
PES(53) ₃	55	55	55	55
PES(48) ₃	48	48	48	48

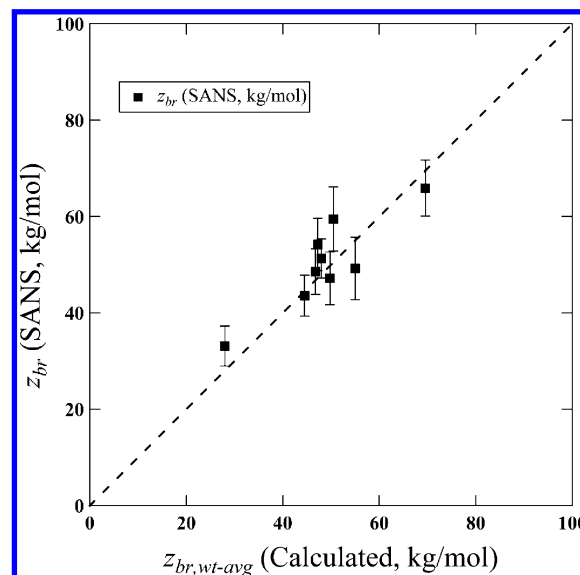


Figure 4. Plot of average branch length, z_{br} , obtained from SANS using eq 7 versus the calculated weight-average arm length, $z_{br,wt-avg}$, from eq 8 for 3-arm star polyethylenes.

that the average branch length measured from the SANS-scaling approach is a weight-average quantity.

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

Table 3. Zero-Shear Rate Viscosity Enhancement for 3-Arm Star Polyethylenes^a

sample	η_0 (Pa·S)	$\eta_0/\eta_{0,L}$
PES(50) ₂ (5)	9.25×10^5	141
PES(50) ₂ (15)	8.56×10^6	1300
PES(50) ₂ (25)	2.28×10^6	347
PES(43) ₃	5.70×10^6	866
PES(15) ₂ (85)	4.60×10^7	6990
PES(40) ₂ (60)	6.42×10^6	976

^aFrom ref 2

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 ,

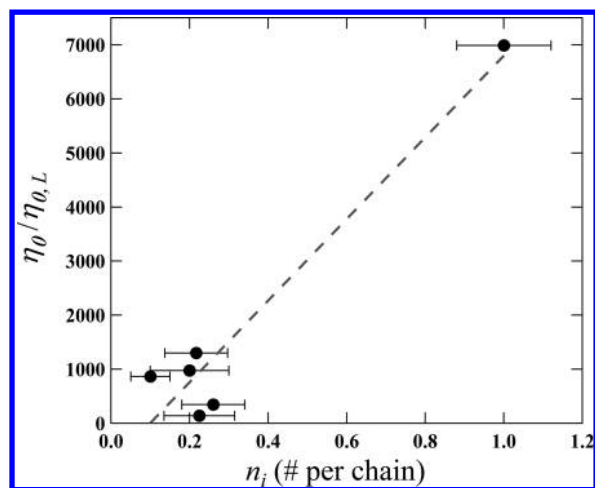


Figure 5. Plot of the zero-shear rate viscosity enhancement, $\eta_0/\eta_{0,L}$, versus the hyperbranch content, n_i , measured from SANS for 3-arm star polyethylenes. A linear behavior is expected based on results shown in ref 5.

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 chemistry¹ have any hyperbranching, the distinctively 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/mol) 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.⁵ The data plotted in Figure 5 can be treated analogous to Figure 4b in ref 5. We can consider the polyethylene melt as a dilute solution of hyperbranched segments in a melt of nonhyperbranched 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 equation³⁰ 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 nonhyperbranched chains. This slope is much higher than the 278 chains/inner segment observed previously for certain metallocene polyethylenes.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.⁵ The 3-arm stars dynamically interact to a greater extent than their linear analogues thereby amplifying the effect of inner segments.

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.³¹ There are limits to this behavior in star polymers as described in the Daoud–Cotton model³² 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, ϕ_{si} that is given by,

$$\phi_{si} = \frac{s_{observed} - s_{unperturbed}}{s_{extended} - s_{unperturbed}} = \frac{z^{1/d_{min}} - z^{3/5}}{z^1 - z^{3/5}} \quad (10)$$

Table 1 lists the ϕ_{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 ϕ_{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_{min} and quantified in ϕ_{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.

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.

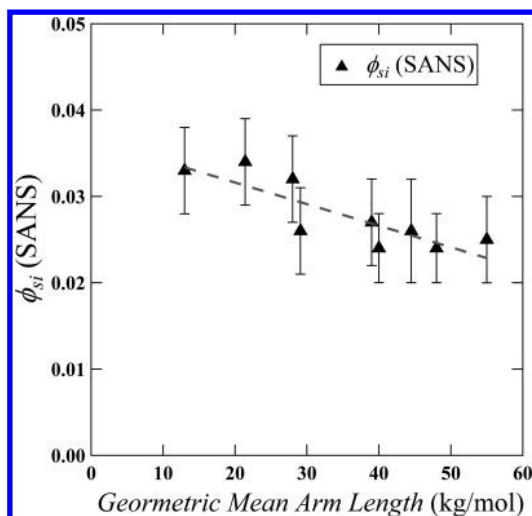


Figure 6. Plot of the steric interaction factor, ϕ_{si} , versus the calculated geometric mean arm length for 3-arm star polyethylenes. The dotted line is a trend line.

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, ϕ_{br} , average long-chain branch length, z_{br} , hyperbranch content, n_v , and steric interaction due to branching, ϕ_{si} . The measurements of ϕ_{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 examples discussed in this article demonstrate 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 polymers¹² and to quantify the degree of folding in proteins and RNA.¹⁰

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