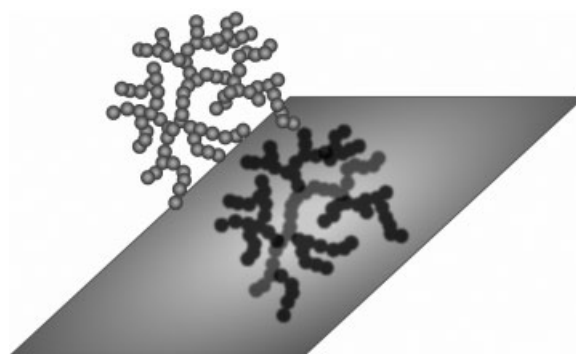


Investigating the Molecular Architecture of Hyperbranched Polymers

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Hyperbranched polymers constitute a unique class of branched macromolecules, where structural complexity is complemented by relative ease of synthesis. The increasing interest in the study of these materials is due to their distinctive properties, inherently tied to their complex molecular architecture, and is augmented by the continual growth of applications like catalysis, viscosity modifiers, and sensors. We report a structural model for HBPs based on fractal scaling of both mass and connectivity. This model is shown to be of use in understanding small angle scattering data, especially in comparison with nuclear magnetic resonance spectroscopy for structural characterization.



Introduction

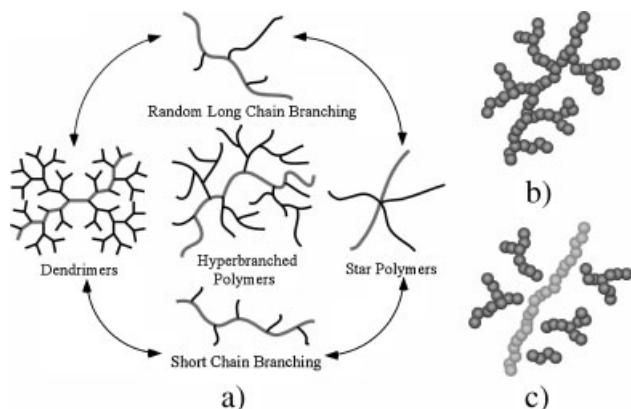
Hyperbranched polymers (HBPs) constitute a special class of macromolecules characterized by their randomly branched topology obtained in a single-step synthesis as opposed to the controlled branching of dendrimers which requires a stringent sequential step synthesis.^[1] HBPs were first synthesized by self-condensation of AB_x type of monomers where $x \geq 2$,^[2] though various alternative synthesis routes^[2a–7b] have been recently developed. The unique properties of HBPs are derived for the most part from their molecular architecture, and has led to many potential applications.^[8a–8d]

HBPs exhibit a hybrid molecular architecture; deriving parts of their structure from a variety of different conventional macromolecular systems [Scheme 1(a)]. In addition to the governing structural parameters like molecular weight, polydispersity, and degree of branching, the large

number of structural isomers of an HBP governs its properties like solubility and glass transition.^[1,2] Along with local degree of branching, the global topology of HBPs (arising from geometrical isomers) is of critical importance. Conventional measures describing the HBP structure using the degree of branching, as put forth by Hawker et al.^[9] based on seminal work in macromolecular systems by Flory,^[10] have been inadequate to completely encompass the plethora of structures associated with the growth of HBP synthesis chemistry.^[11] The degree of branching alone cannot completely characterize the architecture of an HBP.^[12]

Small angle scattering (SAS) of X-rays and neutrons can yield structural information from branched or aggregated systems over multiple size-scales.^[13a,13b] In recent works by Beaucage,^[14] and Kulkarni and Beaucage,^[15] it has been proposed that SAS data could potentially yield topological information from such systems. In this communication, we make an attempt to apply this approach to small angle neutron scattering (SANS) data from the existing literature. It is proposed that this analytic technique could yield a new pathway to describe the topology of HBPs. The details of this analytic approach to obtain information

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Scheme 1. (a) Schematic representation of the hybrid structure of HBPs as discussed in the text, (b) schematic presentation of a branched aggregate formed by the aggregation of primary particles, and (c) the structure of the branched aggregate can be decomposed into the minimum path, and the branched units.

regarding the molecular architecture are explained elsewhere.^[14] The mole fraction branches (MFBs), ϕ_{br} , of any disordered structure of size R_2 [Scheme 1(b) and 1(c)] composed of z primary mer-units of size R_1 can be expressed as^[14]

$$\phi_{br} = \frac{z-p}{z} = 1 - z^{1/c-1} = 1 - \left(\frac{R_2}{R_1}\right)^{d_{min}-d_f} \quad (1)$$

where p is the minimum path [main chain in Figure 1(c)], c the connectivity dimension, d_{min} the dimension of the

minimum path, and d_f the fractal dimension. The parameters in Equation (1) can be obtained from local scattering laws: the Guinier's law [Equation (2a)] and power law [Equation (2b)].^[13b,14]

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

$$I(q) = B_f q^{-d_f} \quad (2b)$$

where $I(q)$ is the scattering intensity, q the scattering vector given as $4\pi/\lambda \sin(\theta/2)$ (λ is the wavelength of the radiation, and θ the scattering angle), G the Guinier prefactor, R_g the mean square radius of gyration, and B_f is the power law prefactor.^[13b,14] The parameter d_{min} can be obtained by a combination of the local scattering laws and is given as^[14]

$$d_{min} = \frac{B_f R_g^{d_f}}{\Gamma\left(\frac{d_f}{2}\right) G} \quad (3)$$

where Γ is the gamma function.

For a branched polymer solution at thermodynamic equilibrium, d_{min} reflects the equilibrated chain scaling normally obtained from d_f for linear chains.^[14] We expect d_{min} to be 5/3 (1.67) for good-solvent conditions and to approach 2 for θ -conditions near where the collapse of the HBP to a globule state is expected. Aggregated or branched systems can be considered to be composed of multiple structural levels, primaries bonding to give an aggregate in

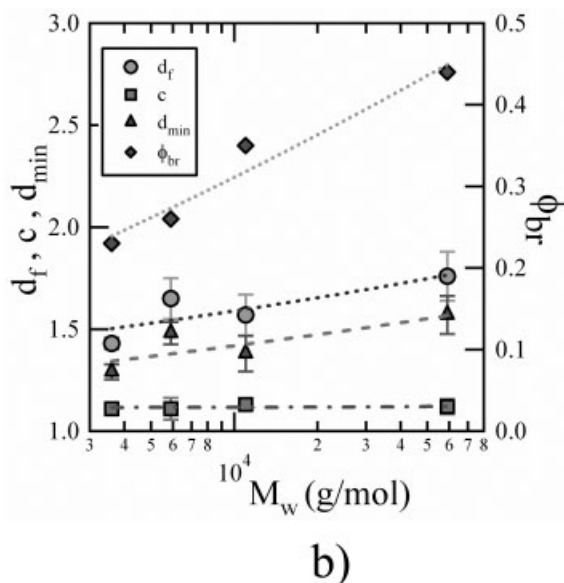
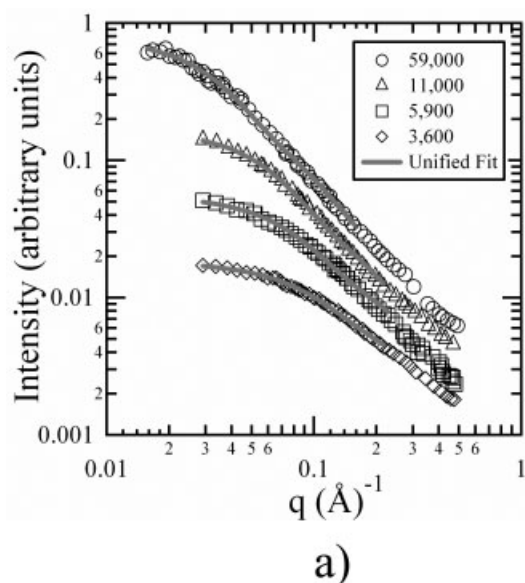


Figure 1. (a) SANS data from hyperbranched poly(ester amide) solutions (1 wt.-%) in tetrahydrofuran- d_4 , from the work of Geladé et al.^[16] The data are fit using the global unified fit,^[13b,17] (legend: sample molecular weight, \bar{M}_w). (b) Fractal dimension d_f , connectivity dimension c , minimum dimension d_{min} , and MFBs ϕ_{br} plotted as a function of the weight-average molecular weight \bar{M}_w .

the case of particulate materials like silica or titania. An analogous description for branched polymers would be Kuhn segment length (a statistical measure of the lower structural level), giving rise to a global structure, that of the overall polymer chain. Such an approach can be applied to branched polymeric systems under the assumption that the Kuhn length constitutes the primaries of these macromolecular materials.^[14] Two systems will be analyzed: scattering data from hyperbranched poly(ester amide) samples, and hyperbranched polyester fractions, which represent comprehensive SANS data sets in the current literature.

Results and Discussion

Hyperbranched Poly(ester amide)s

SANS data representing a series of hyperbranched poly(ester amide) solutions in tetrahydrofuran-*d*4 (1 wt.-%) digitized from the work of Geladé et al.^[16] are shown in Figure 1(a). The data in Figure 1(a) are fit using the global unified fit given by Beaucage.^[13b] The fit results in four parameters, the Guinier prefactor G , the radius of gyration R_g , the mass fractal dimension d_f , and the power law prefactor B_f .^[17,18] Beaucage^[14] showed that from these parameters, d_{\min} and p can be calculated allowing for the determination of ϕ_{br} from Equation (1) since $c = d_f/d_{\min}$.

From these fits [Figure 1(a)], the topological parameters were determined and are listed in Table 1 for a series of samples. The topological dimensions, d_f , c , and d_{\min} , and ϕ_{br} are plotted as a function of the weight-average molecular weight, \bar{M}_w , in Figure 1(b). As explained previously in Equation (1), estimating MFB information in terms of ϕ_{br} requires knowledge of the degree of aggregation, z . Usually this information can be obtained from scattering data if sufficient q -range is observed. Due to the narrow q -range available, the degree of aggregation had to be calculated from the molecular weight information from the work of Geladé et al.^[16] as the ratio of the weight-average molecular weight to the molar mass of the monomeric repeat unit.

Analysis of the topological dimensions (Table 1) obtained from the unified fits [Figure 1(a)] sheds new light on the structure of these HBPs. This dimensional analysis yields a quantitative branch fraction value, ϕ_{br} , as well as additional information on the conformational shape of the HBP molecule as described by the combined information obtained from the dimensions d_f , d_{\min} , and c . The fractal dimension, d_f , increases with the molar mass from 1.43 to 1.76 for samples 1 and 4, respectively. These values are similar to those obtained in the original analysis by Geladé et al.^[16] Interestingly, the connectivity dimension c has very similar values for all four samples, whereas the minimum path dimension, d_{\min} , increases with molecular weight from 1.29 to 1.57 for samples 1 and 4, respectively. For any branched polymer in solution, the minimum path would be expected to mimic the scaling of a linear polymer molecule, assuming that the effect of steric interactions on the scaling of the minimum path arising from the presence of branches is not profound.^[14] The fact that the minimum dimension, d_{\min} , for this set of HBPs approaches the good-solvent scaling of 5/3 (1.67) for a linear polymer chain with increasing molecular weight points in this direction. The branch fraction, ϕ_{br} , increases with molar mass from 0.24 to 0.44.

SAS from macromolecular solutions yields averaged attributes of the global as well as local structural features. This could provide much needed insight in obtaining statistically significant estimates of the topological features of HBPs. Such an analysis could prove especially beneficial, when coupled with nuclear magnetic resonance (NMR) data, as these techniques measure similar aspects of the HBP architecture and could provide complementary information.

Hyperbranched Polyesters

De Luca et al.^[19] conducted a systematic SANS study on a series of fractions of hyperbranched poly[dimethyl-5-(4-hydroxybutoxy)isophthalate] (PDHBI). The data from their work were digitized and fit to the global unified fit,^[13b,17]

Table 1. Details of the hyperbranched poly(ester amide) samples. \bar{M}_w : weight-average molecular weight determined by size exclusion chromatography by Geladé et al.^[16] R_g , d_f , c , d_{\min} , ϕ_{br} , G , and B_f determined from the unified fit^[13b,17] to the scattering data in Figure 1(a). The R_g and d_f values in parentheses are from the work of Geladé et al.^[16] n.a.: not available.

Sample	\bar{M}_w ^[16] g · mol ⁻¹	d_f	c	d_{\min}	ϕ_{br}	z	R_g Å	G	B_f
1	3 600	1.43 (n.a.)	1.11	1.29	0.23	13	17.2 (15.5)	0.069	0.00212
2	5 900	1.65 (n.a.)	1.11	1.48	0.26	21	22.2 (21.6)	0.123	0.00219
3	11 000	1.57 (1.63)	1.13	1.38	0.35	40	26.8 (30.5)	0.256	0.00182
4	59 000	1.76 (1.68)	1.12	1.57	0.44	216	57.5 (n.a.)	0.850	0.00133

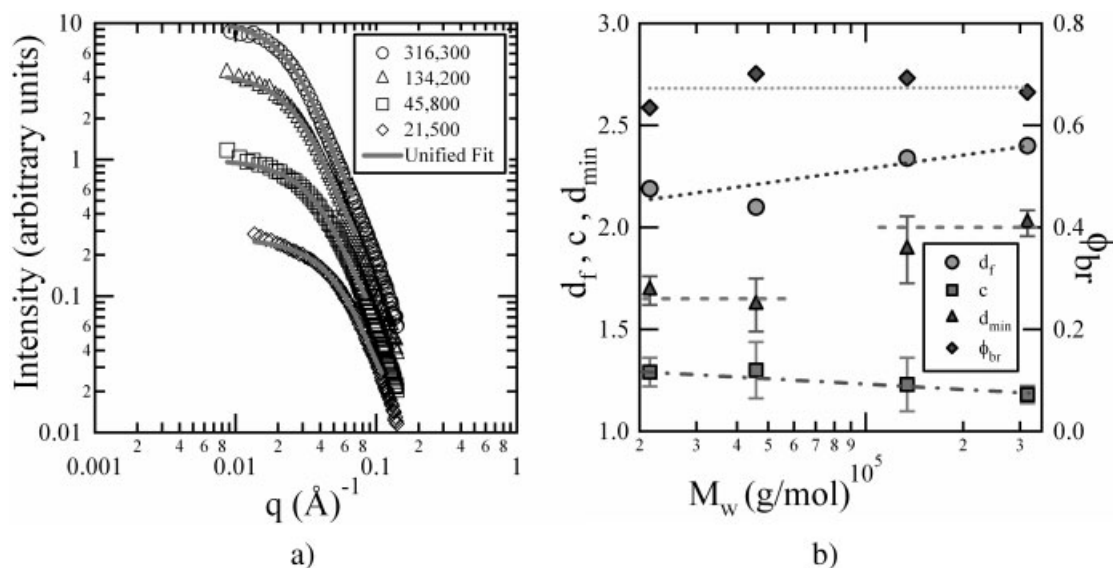


Figure 2. (a) SANS data from hyperbranched PDHBI solutions (2 vol.-%) in tetrahydrofuran- d_4 , from the work of De Luca and Richards.^[20] The data are fit using the global unified fit;^[13b,17] (legend: sample molecular weight, \bar{M}_w). (b) Fractal dimension d_f , connectivity dimension c , minimum dimension d_{\min} , and MFBs ϕ_{br} plotted as a function of the weight-average molecular weight \bar{M}_w .

Table 2. Details of the weight-average molecular weight (\bar{M}_w) of different fractions of hyperbranched PDHBI samples from the work of De Luca and Richards.^[20] d_f , c , d_{\min} , ϕ_{br} , G , and B_f determined from the unified fit^[13b,17] to the scattering data in Figure 2(a).

Fraction	\bar{M}_w ^[20]	d_f	c	d_{\min}	ϕ_{br}	z	R_g	G	B_f
	$\text{g} \cdot \text{mol}^{-1}$						\AA		
10	21 500	2.19	1.29	1.69	0.63	88	30.5	0.53	0.00047
8	45 800	2.10	1.30	1.62	0.70	187	41.7	1.00	0.00061
4	134 200	2.34	1.23	1.89	0.69	550	54.8	1.53	0.00023
2	316 300	2.40	1.18	2.02	0.66	1300	64.9	3.21	0.00027

as shown in Figure 2(a). The topological dimensions [Figure 2(b)] obtained from these fits^a and the molecular weights of these fractions are given in Table 2.

The MFBs, ϕ_{br} , for these fractions are essentially constant, ranging from 0.63 to 0.70 (Table 2). This is a striking difference from the results obtained for the hyperbranched poly(ester amide)s of Geladé et al.^[16] where the MFB increased monotonically with the molecular weight. The MFB for the fractions as obtained from ^{13}C NMR by De Luca and Richards was 0.5 ± 0.1 for all the fractions,^[20] in agreement with the analysis by Feast et al.^[21] Thus the results from both these techniques indicate molecular weight independence of branch content for these fractions. The agreement between SANS and NMR results indicating

^a Note that the low- q fit for these fractions shows a slight divergence.

molecular weight independence of MFB for these fractions validates the SANS analysis presented here, since in this case both these techniques measure similar features of the branched structure, i.e., the molar contribution of the branched species to the total structure. The difference between the two techniques is a consequence of their different definitions of MFB. The MFB estimated by NMR will be an underestimate compared to SANS, since NMR classifies a long chain branch as a linear chain component.^[20,21] For instance, SANS would estimate an MFB of 0.33 for a symmetric 3-arm star polymer, whereas the MFB for such a polymer as estimated by NMR would scale with $1/n$, n being the molecular weight.

Compared to Geladé's samples,^[16] the PDHBI fractions have a higher molar mass ranging from 21 500 to 316 300 $\text{g} \cdot \text{mol}^{-1}$.^[20] These samples also exhibit a higher fractal dimension (2.1–2.4) as would be expected of a highly

branched polymer. The most interesting comparison between the poly(ester amide) samples and the PDHBI fractions arises from the values of the minimum dimension, d_{\min} . As previously stated, the minimum path of a branched polymer would be expected to show the scaling of a linear polymer chain in a solution of the same solvent quality. The lowest molar mass of the PDHBI fractions has comparable molecular weight as the highest molar mass poly(ester amide) samples (Table 1 and 2). Similar to poly(ester amide) sample 4 (Table 1), PDHBI fractions 8 and 10 (Table 2) exhibit a d_{\min} value close to 5/3 (1.67) (good-solvent conditions), though their nonlinearity is apparently higher (higher c). Essentially, as the molecular weight of these fractions increases, the minimum path dimension changes from good-solvent scaling to θ -solvent scaling (fraction 2 has $d_{\min} \approx 2$). This could be explained as poor-solvent conditions due to thermodynamic consequences of branching,^[22] or higher \overline{M}_w effects following Flory-Huggins theory for linear chains.^[10] This could lead to a molecular weight cutoff between good and θ -solvent conditions defined by a d_{\min} transition from 5/3 to 2, Figure 2(b) (triangles).

Equation (1) and (3) are derived for monodisperse systems but can accommodate polydispersity to some extent.^[14] For highly polydisperse samples, we would expect $c < 1$, and for mild polydispersity we would observe smaller than expected values of c and ϕ_{br} so that this analysis would underestimate branch content. However, we have found good agreement in polyolefins with NMR and rheological estimates of branching for polydispersity index as high as 5. Only one of the samples analyzed here has a polydispersity index higher than 5 (Sample 4, Table 1).^[16,20] The analysis is consistent with other data even for this sample ($c = 1.12$).

Conclusion

The growth of interest in the field of HBP synthesis has mainly been fueled by the tremendous potential applications of these materials. The unique architecture of these systems has been characterized in the literature by chromatographic and spectroscopic techniques. In this communication, fractal scaling concepts for mass and MFBs have been combined with SAS data to decipher complementary information about the architecture of these complex systems. A new model for these branched structures is proposed, Figure 1(b) and 1(c). This model when applied to SANS yields ϕ_{br} comparable to values from NMR. It has been shown that branch fraction values, as perceived from NMR analysis or ϕ_{br} values obtained from SANS data can be misleading, and that a more detailed structural analysis manifested in the values of the minimum dimension, d_{\min}

and connectivity dimension, c , can clarify apparent inconsistencies in ϕ_{br} values.

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- [1] Y. H. Kim, O. Webster, "Hyperbranched Polymers", in: *Star and Hyperbranched Polymers*, M. K. Mishra, S. Kobayashi, Eds., Marcel Dekker, New York 1999.
- [2] [2a] C. Gao, D. Yan, *Prog. Polym. Sci.* **2004**, *29*, 183; [2b] Y. H. Kim, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685.
- [3] [3a] Y. H. Kim, O. W. Webster, *Macromolecules* **1992**, *25*, 5561; [3b] C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4583.
- [4] J. M. J. Fréchet, M. Henmi, I. Gitsov, S. Aoshima, M. Leduc, R. B. Grubbs, *Science* **1995**, *269*, 1080.
- [5] M. Liu, N. Vladimirov, J. M. J. Fréchet, *Macromolecules* **1999**, *32*, 6881.
- [6] H. T. Chang, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1999**, *121*, 2313.
- [7] [7a] T. Emrick, H. T. Chang, J. M. J. Fréchet, *Macromolecules* **1999**, *32*, 6380; [7b] C. Gao, D. Yan, *Chem. Commun.* **2001**, *1*, 107.
- [8] [8a] T. Lin, Q. He, F. Bai, L. Dai, *Thin Solid Films* **2000**, *363*, 122; [8b] N. Spetseris, R. E. Ward, T. Y. Meyer, *Macromolecules* **1998**, *31*, 3158; [8c] S. Tanaka, T. Iso, Y. Doke, *Chem. Commun.* **1997**, *21*, 2063; [8d] S. E. Stiriba, H. Kautz, H. Frey, *J. Am. Chem. Soc.* **2002**, *24*, 9698.
- [9] C. J. Hawker, R. Lee, J. M. J. Fréchet, *J. Am. Chem. Soc.* **1991**, *113*, 4583.
- [10] P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca 1953, p. 348.
- [11] D. Yan, A. H. E. Müller, K. Matyjaszewski, *Macromolecules* **1997**, *30*, 7024.
- [12] A. H. Widmann, G. R. Davies, *Comput. Theor. Polym. Sci.* **1998**, *8*, 191.
- [13] [13a] G. Beaucage, H. K. Kammler, R. Mueller, R. Strobel, N. Agashe, S. E. Pratsinis, T. Narayanan, *Nature Mater.* **2004**, *3*, 370; [13b] G. Beaucage, *J. Appl. Crystallogr.* **1995**, *28*, 717.
- [14] G. Beaucage, *Phys. Rev. E* **2004**, *70*, 031401.
- [15] A. S. Kulkarni, G. Beaucage, *J. Polym. Sci., Part B: Polym. Phys.* **2006**, *44*, 1395.
- [16] E. T. F. Geladé, B. Goderis, C. G. de Koster, N. Meijerink, R. A. T. M. van Benthem, R. Fokkens, N. M. M. Nibbering, K. Mortensen, *Macromolecules* **2001**, *34*, 3552.
- [17] G. Beaucage, *J. Appl. Crystallogr.* **1996**, *29*, 134.
- [18] A. Guinier, G. Fournet, "Small-Angle Scattering of X-rays", Wiley, New York 1955.
- [19] E. De Luca, R. W. Richards, I. Grillo, S. M. King, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1352.
- [20] E. De Luca, R. W. Richards, *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 1339.
- [21] W. J. Feast, A. J. Keeney, A. M. Kenwright, D. Parker, *Chem. Commun.* **1997**, *18*, 1749.
- [22] A. S. Kulkarni, G. Beaucage, *Polymer* **2005**, *46*, 4454.