Molecular Characterization of a Hyperbranched Polyester. I. Dilute Solution Properties

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Received 9 June 2002; revised 20 January 2003; accepted 24 January 2003

ABSTRACT: A hyperbranched polyester was fractionated by precipitation to produce 10 fractions with molecular weights between 20×10^3 and 520×10^3 g mol⁻¹. Each of these fractions was examined by size exclusion chromatography, dilute-solution viscometry, intensity, and quasi-elastic light scattering in chloroform solution at 298 K. High-resolution solution-state ¹³C NMR was used to determine the degree of branching; for all fractions this factor was 0.5 \pm 0.1. Viscometric contraction factors, g', decreased with increasing molecular weight, and the relation of this parameter to the configurational contraction factor, g, calculated from a theoretical relation suggested a very strong dependence on the universal viscosity constant, Φ , on the contraction factor. A modified Stockmayer–Fixman plot was used to determine the value of $(\langle r^2 \rangle M_w)^{1/2}$, which was much larger than the value for the analogous linear polymer. The scaling relations of the various characteristic radii $(R_{\rm g}, R_{\rm h}, R_{\rm T}, \text{ and } R_{\eta})$ with molecular weight all had exponents less than 0.5 that agreed with the theoretical predictions for hyperbranched polymers. The exponent for R_{σ} was interpreted as fractal dimension and had a value of 2.38 \pm 0.25, a value that is of the same order as that anticipated by theory for branched polymers in theta conditions and certainly not approaching the value of 3 that would be associated with the spherical morphology and uniform segment density distribution of dendrimers. Second virial coefficients from light scattering are positive, but the variation of the interpenetration function, ψ , with molecular weight and the friction coefficient, k_{0} , obtained from the concentration dependence of the diffusion coefficient suggests that chloroform is not a particularly good solvent for the hyperbranched polyester and that the molecules are soft and penetrable with little spherical nature. © 2003 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 41: 1339-1351, 2003

Keywords: hyperbranched; solution viscosity; light scattering; diffusion;

INTRODUCTION

Dendrimer polymers have attracted considerable interest over the past 10-15 years because of their well-defined structure because of the stringent synthetic procedures that have to be applied.¹⁻⁵ Furthermore, the periphery of dendrimer molecules has many end groups that can be functionalized and used as sites for further chemistry or to interact in a specific manner with their surroundings. The major difficulty associated with dendrimers has already been briefly alluded to above, the demanding and lengthy synthesis procedures that have to be applied to ensure good definition of the molecular structure.

In an effort to overcome this difficulty but to retain the desirable features of dendrimers (their low viscosity and density of chain ends at the

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Journal of Polymer Science: Part B: Polymer Physics, Vol. 41, 1339–1351 (2003) @ 2003 Wiley Periodicals, Inc.

molecular periphery), attention has turned to hyperbranched polymers that can be synthesized by relatively simple 'one pot' methods.^{6,7} This ease of synthesis is gained at the expense of any control or knowledge of the molecular structure or even to what the structure approximates. Aspects such as the degree of branching can be obtained from high-resolution NMR studies, but there are other features that are of interest. Do hyperbranched polymers approach a spherical structure at high molecular weight? Conversely, are they best described as fractal objects with a nonuniform distribution of segments? Is there any correlation between the contraction factors, g' and g, with the degree of branching and/or the molecular weight? Some insight to these various aspects may be obtainable from the classical dilute-solution properties^{8,9} of hyperbranched polymers. In many cases, such techniques may be the only ones applicable because hyperbranched polymers are most commonly amorphous; hence, there is no scope for X-ray crystallography. Furthermore, the necessary deuterated monomers are unavailable; thus, small-angle neutron scattering on the solid state of the polymers is also inapplicable because of the absence of contrast.

We report the results of applying a range of dilute-solution investigations to a series of fractions of a hyperbranched polyester [polydimethyl 5-(4-hydroxy butoxy)isophthalate] and, to a more limited extent, to an analogous linear polymer. The information content of the various parameters discussed is first set out before moving to the experimental, results, and discussion sections.

THEORETICAL BACKGROUND

The understanding of the behavior of linear, flexible polymers in dilute solution and the consequent development of theories that provides the molecular explanation of the observed properties is now very deep and at a sophisticated level.⁸⁻¹¹ The basis for this understanding was laid some 30-60 years ago by the many investigations of the dilute-solution properties of linear polymers that provided global properties of the polymer molecules and their relation to molecular weight and structural features of the molecular. Notwithstanding the important role of molecular weight (and its distribution) in determining the global properties, the factors of major influence are the molecular structure and the space occupied by the molecule that define properties in solution and in the solid state.

The last statement is even more pertinent to branched polymers that clearly have very different properties as compared with linear polymers of the same molecular weight. However, examination of the global properties for such polymers has been mainly confined to star polymers¹²⁻¹⁴ with some notable exceptions where highly branched naturally occurring polymers have been discussed. Global parameters that are of value in addressing the molecular level behavior of branched polymers are provided by viscometry and scattering techniques, light scattering being particularly valid. The particular parameters are the intrinsic viscosity $([\eta])$, the radius of gyration (R_{α}) , the second virial coefficient (A_2) , and the z-average diffusion coefficient at infinite dilution (D_{o}) . From these parameters other radii can be constructed-the thermodynamic, hydrodynamic, and viscosity radii. The latter two provide insight on the interaction of the polymer with the solvent, whilst in motion and comparison with values for the linear polymer can be helpful in understanding the branched polymer structure. The thermodynamic radius responds to the regions of interaction between two polymer molecules, that is, the excluded volume and comparison with the hydrodynamic radius provide an estimate of which factor operates over a longer range. The interpenetration function^{8,9} (Ψ) is composed from A_2 , the molecular weight, and R_g and is a quantitative measure of the degree of interpenetration of polymer molecules in dilute solution. The molecular weight dependence of these radii differs for branched structures as compared with linear equivalents, and the scaling exponents can either be used to assess the fractal nature of the branched polymers or compared with theoretical predictions for model or simple limiting structures, for example, spherical molecules or flexible Gaussian coils. Additionally, the dimensionless ratios (e.g., Ψ and ratios of the various radii and the combination $A_2 M_w/[\eta]$) often approach asymptotic values, and comparison with the values for linear polymers or polymers with precisely defined architecture can aid in the interpretation of branched polymer behavior.

All of these parameters have been used in the ensuing discussion of the hyperbranched polyester, parameters that are much used are the contraction or branching factors, g' and g.^{15,16} The former is the ratio of the intrinsic viscosity of the branched polymer to that of the linear polymer of



Figure 1. Representation of the monomer from which PDHBI was synthesized.

equal molecular weight; the latter is formed from the ratio of the mean square radii of gyration of the two polymers. Relationships between the two contraction factors have been attempted mainly on the basis of data for star polymers. In the absence of radii of gyration data for the analogous linear polymer (see below), we have used some of the relationships to examine the connection between g' and the calculated values of g.

EXPERIMENTAL

Synthesis

Hyperbranched Polymer, Polydimethyl 5-(4-Hydroxybutoxy)isophthalate (PDHBI)

Figure 1 shows the monomer from which the hyperbranched polymer PDHBI was synthesized. The details of this synthesis have been provided elsewhere¹⁷ and are not repeated here. At the completion of polymerization (100% conversion), the polymer was a transparent, vitrified mass with a pale brown color. On dissolution in chloroform and reprecipitation in excess methanol followed by filtering and drying, a white powder was obtained. Thermal analysis suggested this polymer to be amorphous, the only transition observed being a glass transition at 307.8 K.

A variety of molecular weight fractions were obtained from this parent polymer by adding methanol to a continuously stirred 5% solution of the polymer in toluene (a slightly poorer solvent than chloroform). When the solution was judged to be sufficiently turbid, no additional methanol was added, and its temperature was raised until a clear solution was obtained. At this point stirring was stopped, and the solution was allowed to cool overnight to 298 K. The precipitated polymer settled to the bottom of the fractionation vessel and was removed. By repeating this procedure a total of 10 separate fractions was obtained.

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Analogous Linear Polymer, Polybutoxybenzoate (PBB)

Methyl 3-(4-hydroxybutoxy)benzoate was meltpolymerized under a constant flow of nitrogen with antimony(III) oxide and manganese(II) acetate as catalysts with added triphenyl phosphate as a thermal-degradation inhibitor. The polymer obtained was dissolved in chloroform and precipitated in excess methanol. Samples of this polymer were transesterified in the presence of titanium butoxide at 473 K under vacuum for different times to increase the molecular weight. By this means, four samples of a linear polymer were obtained with weight-average molecular weights $(M_{\rm w}'s)$ in the range $7000 \le M_{\rm w}/g \text{ mol}^{-1} \le 51,000$. Unlike the hyperbranched polymer, PBB was semicrystalline with a glass-transition temperature (T_g) of 285.7 K, a crystallization temperature of 328.0 K, and a melting point of 398.6 K.

Dilute-Solution Characterization Methods

Size Exclusion Chromatography (SEC)

All fractions of hyperbranched and linear polymers were analyzed by SEC with chloroform as the eluting solvent, triple detection (refractive index, viscosity, and right-angle light scattering) being used at all times. To ensure that the molecular weights were as accurate as possible, the specific refractive-index increment at the wavelength of the light source used (670 nm) was obtained from a Cauchy dispersion plot of values experimentally obtained for both linear and hyperbranched polymers at light wavelengths of 436, 488, 546, and 633 nm.

Dilute-Solution Viscometry

Intrinsic viscosities of PDHBI and PBB in chloroform solution at 298 K were obtained with a Schott AVS 350 automatic viscometer with automatic dilution, the data being interpreted via Huggins' plots.

Light Scattering

 $M_{\rm w}$'s, $R_{\rm g}$'s, and A_2 's for solutions of the hyperbranched polymer in chloroform were obtained from Zimm plots of Rayleigh ratio data. These latter were obtained with a Malvern 4700 goniometer and an argon ion laser ($\lambda_o = 488$ nm) operating at 75 mW. Solutions were filtered through 0.22 μ m filters and visually inspected in the beam to ensure they were dust free. Statistical errors on the molecular parameters obtained were typically $\pm 5\%$ on M_w , $\pm 15\%$ on R_g , and $\pm 10\%$ on A_2 .

Quasi-elastic light scattering data were collected under the same conditions with a Brookhaven BI-9000 AT correlator and a 35-mW He–Ne laser ($\lambda_0 = 633$ nm). Correlation functions were analyzed by nonlinearly least-squares fitting the cumulants expression to the data

$$G(au) = \exp\!\left[2\!\left(\!c_{\mathrm{o}} - \Gamma au + rac{K au^2}{2}\!
ight)\!
ight] + G(\infty)$$

where $G(\tau)$ is the value of the correlation function at a delay time, τ , $G(\infty)$ being the base line or 'far point' value; and Γ and K are the first and second cumulants with

$$\Gamma = D\mathbf{Q}^2$$

 $K = \langle (\Gamma - \langle \Gamma \rangle)^2
angle D\mathbf{Q}^2$

with **Q**, the scattering vector, defined as $(4\pi \tilde{n}_o/\lambda)\sin\theta$ for a solvent with refractive index \tilde{n}_0 and light scattered at $2\theta^o$ to the incident beam direction. Values of the diffusion coefficient obtained over a range of solution concentrations were used to obtain the infinite dilution value, D_o , by extrapolation according to the equation 18

$$D(c) = D_{\rm o}(1 + k_{\rm D}c \cdots) \tag{1}$$

and D_0 is the *z*-average diffusion coefficient.

Light scattering experiments were also attempted on solutions of the linear polymer in chloroform; however, it became evident that some form of aggregation of the linear polymer takes place in solution (see below), and these data could not be taken to be those for molecularly dispersed solutions.

RESULTS

Hyperbranched Polymer

Degree of Branching

Figure 2 indicates the carbon atoms in PDHBI for which we anticipate different resonances in the



Figure 2. Carbon atoms in PDHBI that produce the observed ¹³C NMR signals associated with linear, branched, and terminal units.

¹³C NMR spectra. A typical example of a fragment of the ¹³C NMR spectrum for one of the fractions obtained is displayed in Figure 3. The spectrum was curve-fitted, and the fitted curve deconvoluted into the individual Gaussian curves shown. Attribution of each peak to a particular carbon atom was made with the full widths at half-height, this factor being proportional to the mobility of the carbon atoms and larger full widths at half-height being associated with reduced mobility. A priori, we expect branched units in PDHBI to be the least mobile and terminal units to be the most mobile with the linear carbon atoms having mobilities in between these values. On this basis, we have labeled the individual curves as terminal (T), linear (L), or branched (B)—the integral of each unit in the polymer. These integrals can be used to calculate the degree of branching (D_b) of the polymer with definitions of this parameter by Hawker and Frechet¹⁹

$$D_{\rm b} = \frac{B+T}{B+T+L}$$

or that of Holter et al.²⁰

$$D_{\rm b} = \frac{2B}{2B+L}$$

Values of $D_{\rm b}$ obtained for all the fractions exhibited no dependence on fraction molecular weight within the uncertainty associated with the curve-fitting and deconvolution procedure—the value observed being 0.5 \pm 0.1, regardless of which equation was used to calculate $D_{\rm b}$.



Figure 3. Observed ¹³C NMR signal and its deconvolution and subsequent reconstruction: 1 terminal carbon, 2 branched carbon, and 3 linear carbon (double peak because of the two differing carbon environments on the linear units).

Light Scattering

Both classical intensity and quasi-elastic light scattering experiments were made on solutions of the PDHBI fractions in chloroform. Interpretation of the intensity data was enabled by separate measurements of the specific refractive-index increment (dn/dc) at a wavelength of 488 nm; at 298 K the value obtained was 0.13 ± 0.01 cm³ g⁻¹. Values of $M_{\rm w}$, root-mean-square $R_{\rm g}$, and A_2 for all fractions are given in Table 1, which also includes the diffusion coefficients and the slope factor $k_{\rm D}$ as well as the hydrodynamic radius $R_{\rm h}$ from the Stokes–Einstein relationship.

SEC and Viscometry Data

Molecular weight averages and the intrinsic viscosity obtained from the triple-detection SEC are given in Table 2, which also includes the intrinsic viscosities obtained by automatic viscometry so that a direct comparison can be made. The first, highest molecular weight fraction has a large polydispersity (4), and this clearly has an influence on some of the succeeding parameters obtained from the dilute-solution data, with values being observed for this fraction that do not follow the trend for the lower-molecular-weight and narrower polydispersity fractions.

Table 1. Molecular Weight, R_g , A_2 , D_0 , k_D , and R_h Data Obtained from Light Scattering Data on Hyperbranched Fractions of PDHBI in Chloroform at 298 K

Fraction	$M_{ m w}/10^3~{ m g~mol^{-1}}$	$R_{ m g}/10^{-7}~{ m cm}$	A_2 /cm 3 mol g $^{-2}$	$D_0/10^{-7}~{ m cm}^2~{ m s}^{-1}$	$k_{ m D}/{ m mL~g^{-1}}$	$R_{ m h}/10^{-7}~{ m cm}$
1	510.8	20.2	0.11×10^{-3}	2.00	12.9	10.5
1	515.8	50.5	$0.11 \times 10^{\circ}$	2.09	10.2	19.0
2	328.2	20.3	$0.34 imes10^{-3}$	3.30	24.3	12.4
3	154.0	14.0	$0.67 imes10^{-3}$	3.70	34.4	10.4
4	142.9	13.6	$0.67 imes10^{-3}$	4.12	41.6	9.5
5	118.5	15.6	$0.87 imes10^{-3}$	4.68	40.4	8.7
6	83.7	11.9	$1.03 imes10^{-3}$	4.13	43.6	9.9
7	63.5	13.9	$0.77 imes10^{-3}$	4.57	44.1	8.9
8	47.6	8.5	$1.19 imes10^{-3}$	5.47	43.7	7.5
9	36.0	14.0	$1.12 imes10^{-3}$	8.13	50.6	6.5
10	20.2	7.1	$1.41 imes10^{-3}$	8.83	45.6	4.9

Fraction	$M_{ m n}$ /g mol $^{-1}$	$M_{ m w}/{ m g}~{ m mol}^{-1}$	$M_{ m w}/M_{ m n}$	$[\eta]$ /ml g $^{-1}$	$[\eta]^2/\mathrm{ml}~\mathrm{g}^{-1}$
1	102,300	452,800	4.4	54.5	60.4
2	130,500	316,300	2.4	48.5	60.4
3	92,700	149,100	1.6	36.5	37.9
4	71,700	134,200	1.8	34.2	37.6
5	45,900	100,300	2.1	31.9	33.6
6	50,700	75,900	1.5	28.8	28.9
7	44,400	62,900	1.4	25.6	27.1
8	30,400	45,800	1.5	23.5	24.8
9	27,900	35,200	1.2	20.6	21.6
10	16,800	21,500	1.2	16.9	18.3

Table 2. Molecular Weights and Intrinsic Viscosities Obtained by SEC on PDHBI Fractions in Chloroform

^a Values obtained by dilute-solution viscometry.

Linear Polyester

All the dilute-solution characterization methods applied to the hyperbranched polymer (viscometry, light scattering, and SEC) were also applied to each of the four fractions of the analogous linear polymer in chloroform solution at 298 K. Average molecular weights and intrinsic viscosities from SEC, viscometry, and light scattering are given in Table 3. The light scattering values of $M_{\rm w}$ are larger than those obtained by SEC. Because just slightly negative second virial coefficients were observed for these solutions, indicating poor solvent conditions, we attribute these higher molecular weights to the presence of some aggregates in the solutions. Light scattering being more responsive to higher-molecular-weight species will be biased by their presence and give a higher molecular weight. However, SEC molecular weights depend on separation by hydrodynamic properties, and, moreover, the concentration of polymer in the solutions during the SEC process is considerably less, making the solution thermodynamics more favorable. Consequently, we used the SEC-derived molecular weights and intrinsic viscosities for the linear polymer, these

values being more characteristic of molecular solutions of the linear polymer. We note in passing that the intrinsic viscosity of solutions of the linear polymer obtained by classical viscometry was little different from the values provided by SEC analysis and triple detection, that is, either the capillary flow was sufficient to break up the aggregates or they were present in only very small amounts.

DISCUSSION

Contraction or Branching Factors and Unperturbed Dimension

From a linear least-squares fit to the intrinsic viscosity and light scattering $M_{\rm w}$ data plotted in Figure 4, the Kuhn–Mark–Houwink–Sakurada equation obtained is

$$[\eta] = (0.36 \pm 0.05) M_{\rm w}^{(0.39 \pm 0.02)} / \text{mL g}^{-1}$$

and we note that the exponent is much smaller than typical values encountered for linear poly-

Sample	$M_{ m n}/{ m g\ mol^{-1}}$	$M_{ m w}$ /g mol $^{-1}$	$M_{ m w}/M_{ m n}$	$[\eta]/\mathrm{ml}~\mathrm{g}^{-1}$	$M_{ m w}^{ m a}/ m g\ mol^{-1}$	$[\eta]^{ m b}/ m ml~g^{-1}$
1	22,100	51,000	2.3	42.7	148,600	47.7
2	14,600	27,200	1.8	24.4	50,800	26.3
3	9,200	12,100	1.3	27.6	46,450	24.7
4	5,400	7,400	1.3	14.8	23,300	20.2

Table 3. Molecular Weights and Intrinsic Viscosities for the Linear Polyester Sample from SEC in Chloroform

^a Obtained from dilute-solution light scattering.

^b Obtained from dilute-solution viscometry.

mers but is in the range anticipated for hyperbranched polymers.²¹ Polysaccharide polymers have often been cited as naturally occurring examples of hyperbranched polymers. Ioan et al.²² examined glycogen fractions and the viscosity exponent noted was 0.4—these fractions being obtained by degradation of starting material had a very wide range of polydispersities with large values from 29 to 6.

An equivalent Mark–Houwink analysis of the intrinsic viscosity data for the linear polyester gives

$$[\eta] = (0.21 \pm 0.2) M_{
m w}^{0.49 \pm 0.1}$$

and suggests that at 298 K in chloroform, this polymer is in near-theta or unperturbed conditions, an assertion that is confirmed by the slightly negative second virial coefficients obtained.

With these relationships for the hyperbranched and linear polymers established, we can obtain values of the contraction or branching factor, g', and a double log plot of these values as a function of the molecular weight of PDHBI is depicted in Figure 5, the scaling relation being g'= $(2.1 \pm 0.2) M_{\rm w}^{-0.12\pm0.01}$. Contraction factors were originally defined in terms of the mean square radii of gyration of the linear and branched polymers^{15,16}

$$g = R_{\rm gb}^2 / R_{\rm gl}^2 \tag{2}$$

and hence



Figure 4. Kuhn–Mark–Houwink–Sakurada plot for PDHBI fractions in chloroform at 298 K with light scattering and dilute-solution viscometry data.



Figure 5. Relation of the contraction ratio g' to the fraction molecular weight.

$$g' = \frac{\Phi_{\rm b}}{\Phi_{\rm l}} g^{3/2} = \Phi^* g^{3/2} \tag{3}$$

where the possible increase in the magnitude of the universal viscosity constant, Φ , because of the increased segment density in hyperbranched polymers is incorporated. In the absence of values for the radius of gyration of the linear polymer, we can make no estimate of the values of g; thus, we are unable to estimate the dependence of Φ^* on g. We can, however, make some progress with the expression for g proposed by Zimm and Stockmayer¹⁵ for branched polymers with trifunctional branch points, for example, the AB₂ type of monomers used to synthesize PDHBI. For fractionated polymer, the average value of g depends on the average number of branched units, m, in a hyperbranched material

$$\langle g(m) \rangle = \left[\left(1 + \frac{m}{7} \right)^{1/2} + \frac{4m}{9\pi} \right]^{1/2}$$
 (4)

and

$$m = rac{M_{
m w}}{m_{
m o}} D_{
m b}$$

where m_0 is the molecular weight of the trifunctional AB₂ molecule. From calculated values of $\langle g(m) \rangle$, the plot in Figure 6 was obtained and the least-squares fit gives

$$g' = (0.86 \pm 0.03) \langle g(m) \rangle^{0.26 \pm 0.02}$$



Figure 6. Contraction factor g' plotted as a function of the g contraction factor calculated from the theoretical relation of Zimm and Stockmayer.

Evidently, the exponent is far smaller than the value of 0.5 originally suggested by Zimm and Kilb²³ or the exponent of 0.6 suggested on an empirical basis by Kurata et al.²⁴ and far smaller than the exponent of 0.9 that Weissmuller and Burchard²⁵ obtained on the basis of the analysis of data available for star polymers. This reduction in the exponent is attributed to the dependence of Φ^* on g, and to recover $g' \alpha g^{3/2}$, this suggests that $\Phi^* \sim g^{-1.25}$, that is, very strong g dependence.

A major use of intrinsic viscosity has been for the evaluation of unperturbed dimensions. Where theta conditions are either unknown or unobtainable, the Stockmayer–Fixman relation²⁶ is often used

$$\frac{[\eta]}{M_{\rm w}^{1/2}} = K_{\theta} + 0.51 \Phi_{\rm o} B M_{\rm w}^{1/2} \tag{6}$$

where

$$K_{ heta}=\Phi_{
m o}\!\left(\!rac{\langle r^2
angle}{M_{
m w}}\!
ight)^{\!\!3/2} \hspace{0.4cm} ext{and} \hspace{0.4cm} B=2arbla^2\!(1+2\chi)\!/\!V_1\!N_{
m A}$$

where ν is the polymer specific volume, χ is the polymer–solvent interaction parameter, V_1 is the molar volume of the solvent, and Φ_0 is the universal viscosity constant with a value of 2.87×10^{23} when $[\eta]$ is in units of milliliters per gram. For the linear polymer analogous to PDHBI, there is no need to use this expression for the chloroform solution data because the solutions are effectively at theta conditions, and the prefactor in the Mark–Houwink relation can be used directly. From the value of $K_{\theta} = 0.21$ mL g⁻¹ we obtain $(\langle r^2 \rangle_0 / M_w)^{1/2} = 9 \times 10^{-9}$ cm.

The Stockmayer-Fixman plot developed for linear polymers is not directly applicable to hyperbranched polymers; plots with negative slopes are obtained suggesting that χ is large and negative. Although this may be true for some polymersolvent combinations this is not the case here because A_2 values are large and positive; the real reason lies in the need for different exponents for the molecular weights. The general relationship between intrinsic viscosity and molecular weight for highly branched polymer proposed by Zimm and Kilb²³ is

$$[n] = KM^{\{[(1+3\varepsilon)/2]-1/4\}}$$

For theta conditions $\epsilon = 0$ and hence

$$[\eta]_{\theta} = K_{\theta} M^{1/4}$$

For solvent conditions other than theta conditions, we have

$$[\eta] = [\eta]_{\theta} \alpha^3$$

but we can also write a general relation for the expansion factor as

$$\alpha^3 = 1 + BM^{1/2}/K_{\theta}$$

and hence

$$[\eta] = K_{ heta} M^{1/4} + B M^{3/4}$$

that is

$$[\eta]/M^{1/4} = K_{\theta} + BM^{1/2} \tag{7}$$

and a plot on the left-hand side of eq 7 as a function of $M^{1/2}$ should be linear. However, the relation for $(\langle r^2 \rangle_o / M_w)^{3/2}$ is based on a constant value of Φ_b in K_{θ} , and because we noted the strong dependence of Φ_b on g above it is possible that the plot obtained could be highly nonlinear. In reality for our data plotted in Figure 7 we obtain a linear plot over a molecular weight range of PDHBI from 20,000 to 150,000 g mol⁻¹. At this point, we note that as well as a g dependence on the value of Φ_b , there may also be a molecular weight dependence. Pre-empting the discussion on fractal dimensionality to come later, the scaling relation



Figure 7. Modified Stockmayer–Fixman plot for hyperbranched polymers with the data for PDHBI.

between intrinsic viscosity and molecular weight can be written as

$$\lceil \eta \rceil = KM^{a_{\Phi} + (3/d_{\mathrm{f}} - 1)}$$

where a_{Φ} expresses the molecular weight dependence of $\Phi_{\rm b}$, and $d_{\rm f}$ is the fractal dimension. We demonstrate below that $d_{\rm f} = 2.38$, and because the exponent for the molecular weight dependence is 0.39, then $a_{\Phi} = 0.13$, that is, the value of $\Phi_{\rm b}$ increases with molecular weight and this will offset the decrease because of the g dependence. Because of the absence of knowledge of the constant of proportionality in the scaling relation $\Phi_{\rm b}$ $\propto M^{a_{\Phi}}$, we are unable to calculate $\Phi_{\rm b}$, but given the opposing influences of g and molecular weight on $\Phi_{\rm b}$ we tentatively use the value for $\Phi_{\rm lin}$, that is, 2.87 \times 10²³, and this gives $(\langle r^2 \rangle_0 / M)^{1/2} = 16.97 \times$ 10^{-9} cm. Evidently, the meaning of an end-to-end distance for a hyperbranched polymer is moot; consequently we interpret $(\langle r^2 \rangle_0 / M)^{1/2}$ as an effective value for comparison with that for the linear polymer. The value is circa twice that of the analogous linear polymer and is a reflection of the reduction in the available minimum energy rotational states because of the high extent of branching in PDHBI that would lead to a highly extended configuration in a linear polymer of the same molecular weight.

Molecular Dimensions and Generalized Ratios for the Hyperbranched Polymer

In addition to the radius of gyration and hydrodynamic radius that are obtainable more or less directly from intensity and quasi-elastic light scattering, there are other parameters related to the size of the hyperbranched polymer molecule. These are the thermodynamic radius

$$R_{\rm T} = \left(\frac{3}{16\pi} \frac{A_2 M_{\rm w}^2}{N_{\rm A}}\right)^{1/3}$$

and the viscosity radius

$$R_{\eta} = \left[\frac{[\eta]M}{(10\pi/3)N_{\rm A}}\right]^{1/3}$$

These various radii are plotted as a function of the PDHBI fraction molecular weights in Figure 8. Least-squares fits to the data provide the relations below, with all radii in centimeters

$$R_{\sigma} = 1.1 \times 10^{-8} M_{\rm w}^{0.42 \pm 0.05} \tag{8}$$

$$R_{\rm h} = 1.52 \times 10^{-8} M_{\rm w}^{0.36 \pm 0.04} \tag{9}$$

$$R_{\rm T} = 6.65 \times 10^{-9} M_{\rm w}^{0.44 \pm 0.04} \tag{10}$$

$$R_n = 3.9 \times 10^{-9} M_{\rm w}^{0.46 \pm 0.01} \tag{11}$$

The exponent in the relationship between R_{a} and molecular weight can range between values of 0.33 for a spherical object with uniform mass distribution to 1.0 for a rigid-rod particle. Such clear-cut interpretation can be complicated by thermodynamic effects leading to chain expansion. Although the R_g exponent observed of 0.42 suggests that PDHBI molecules are approaching spherelike behavior, greater insight into the nature of the hyperbranched polymer can be obtained by interpreting the exponent as a fractal dimensionality $(d_{\rm f})$ that is the reciprocal of the exponent in eq 8, that is, $d_{\rm f} = 2.38 \pm 0.25$. For linear polymers with a Gaussian coil nature, values of $d_{\rm f}$ range from 1.66 to 2 for thermodynamically good and theta solvent conditions, respectively, reflecting the well-known excluded volume exponents of ~ 0.6 and 0.5 for these two conditions.¹⁰ For branched polymers, $d_{\rm f}$ is predicted to have the values of 2 and 2.28 for randomly branched polymers in good and theta solvent conditions, respectively,^{27–29} although values of 3 have been observed for some dendrimers³⁰ suggesting a uniform distribution of segments in the space pervaded by the polymer. The value observed here suggests that the hyperbranched polymer has a geometry lying somewhere be-



Figure 8. Characteristic radii as a function of molecular weight for PDHBI fractions in chloroform at 298 K: (a) radius of gyration, (b) hydrodynamic ratio, (c) thermodynamic radius, and (d) viscosity radius.

tween that of a sphere $(d_f = 3)$ and a disk $(d_f = 2)$. Perhaps the most well discussed highly branched polymers have been the naturally occurring polymers glycogen and amylopectin, with glycogen having a fractal dimensionality of 2.86.³¹ However, starches from various sources (and thus differing contents of amylose and amylopectin) have rather smaller values of $d_{\rm f}$ (~2.4) approximating to that of a nonswollen cluster although the second virial coefficients were positive. Geladé et al.³² obtained fractal dimensions for hyperbranched polyesteramides from the scattering vector dependence of small-angle neutron scattering from solutions in deutero tetrahydrofuran, an average value of 2.04 being obtained that agreed with that predicted when hyperbranched polymers are in good solvent conditions. However, the polyesteramides were unfractionated and had particularly large polydispersities, up to 87 in one case, and this will influence the values of $d_{\rm f}$.

Certain combinations of dilute-solution parameters form dimensionless ratios that have characteristic values for particular situations. In addition to the ratio of the various radii, the interpenetration function, Ψ , is included

$$\Psi = rac{A_2 M_{
m w}^2}{R_{
m g}^3 4 \, \pi^{3/2} N_A}$$

Table 4 sets out these dimensionless ratios and the values predicted by theory and observed for linear and 18-arm star polymers in good and

	$R_{\mathrm{T}}/R_{\mathrm{g}}$	$R_{ m h}/R_{ m g}$	$R_{\eta}/R_{ m g}$	$R_{\eta}\!/\!R_{ m h}$	Ψ
Self-avoiding	0.60	0.64	0.73	1.14	0.269
Random walk					
Unperturbed		0.81	0.82	1.02	
Gaussian coil					
Hardsphere	1.29	1.29	1.29	1.00	1.61
Linear polybutadiene					
Good solvent	0.71	0.72	0.84	1.17	
theta solvent	_	0.74	0.84	1.13	—
18-arm star polybutadiene					
Good solvent	1.19	1.11	1.21	1.08	1.1
Theta solvent		1.18	1.21	1.03	

Table 4. Predicted and Observed Values for Dimensionless Ratios

theta solvent conditions. Figure 9 displays the values obtained for the four radii ratios; the data point for the highest molecular weight fraction is generally anomalously low, attributable to the broad molecular weight distribution of this fraction (4). Although the data are somewhat scattered, the general feature is an increase in the magnitude of each ratio approaching an asymptotic value. None of these asymptotic values approach that predicted for a hard sphere; the ratios $R_{\eta}/R_{\rm g}$ and $R_{\rm h}/R_{\rm g}$ are closer to the predicted values for a self-avoiding random walk, whereas $R_{\rm T}/R_{\rm g}$ is somewhat closer to that for a hard sphere it is still sufficiently distant that there is probably little

hard sphere character to PDHBI. Values of $R_{\eta}/R_{\rm h}$ are far too scattered to make meaningful conclusions, and as Table 4 shows, the range of values for this parameter is not wide enough for very different situations. The experimentally observed interpenetration function values are very scattered and generally increase as the molecular weight increases, eventually exceeding the excluded volume limit value of 0.269 for a linear chain but still significantly smaller than the hard sphere limit although no definitive conclusions can be made from this parameter. The ratio $A_2M_{\rm w}/[\eta]$ also shows a rapid increase with molecular weight (Fig. 10) but with no evidence for an



Figure 9. Figure 9. Ratios of radii as a function of molecular weight.

asymptotic value being approached. Asymptotic values of 1.07 (linear polymer) and 1.6 (hard sphere) are predicted for this ratio, but they increased with branching in star polymers and exceeded the value for a hard sphere.¹¹ Evidently, the values we observe here conform to this behavior because the ratio is considerably larger than that for a hard sphere and reflects the highly branched nature of the polymer. We note that the dependence of $A_2 M_w/[\eta]$ reflects that of the interpenetration function, Ψ . Because

$$rac{A_2 M_{
m w}}{[\eta]} = rac{\pi^{1/2} 6 \Psi}{5 \Phi}$$

it appears that the difficulty of interpenetration of the segment clouds on hyperbranched molecules becomes dominant at high molecular weights, whereas the smaller solvent molecules are easily able to penetrate the volume pervaded by the hyperbranched polymer molecule.

Concentration Dependence of Diffusion Coefficients and the Friction Coefficients

Having applied the diffusion coefficients to calculate $R_{\rm h}$ discussed above, we now turn our attention to the concentration dependence of the diffusion coefficients, particularly the values of $k_{\rm D}$ in eq 1. This hydrodynamic parameter is related to the thermodynamic parameters by the equation

$$k_{\rm D} = 2A_2M_{\rm w} - k_{\rm s} - \bar{v}$$

3.0

2.5

 $[h]^{M}W^{2}W$

1.5

1.0

1E4

0



1E5

M_



Figure 11. Friction concentration coefficient, k_o , obtained for each molecular weight fraction of PDHBI.

where \bar{v} is the partial specific volume, and $k_{\rm s}$ is a term in the concentration dependence of the friction coefficient

$$f(c) = f_{\rm o}(1 + k_{\rm s}c + \cdots)$$

and

$$k_{\rm s} = k_{\rm o} (4\pi R_{\rm h}^3 N_{\rm A}/3M)$$

where $k_{\rm o}$ was calculated to have values of 2.23– 7.16 for linear polymer in theta and good solvent conditions, respectively,¹⁸ the latter value also being the hard sphere limit. The values quoted pertain to values of $k_{\rm D}$, $k_{\rm s}$, and so forth where the concentration is expressed in volume fraction, that is

$$k_{\mathrm{D}}^{\phi}=rac{3k_{\mathrm{D}}M_{\mathrm{w}}}{4\pi N_{\mathrm{A}}R_{\mathrm{h}}^3}$$

and

$$k_{\mathrm{s}}^{\phi} = rac{8R_{\mathrm{T}}}{R_{\mathrm{h}}} - k_{\mathrm{D}}^{\phi}$$

Values of $k_{\rm o}$ obtained are very scattered (Fig. 11) but do exhibit a trend to increasing values as the hyperbranched polymer molecular weight increases (as does the ratio $R_{\rm T}/R_{\rm h}$). In this respect, the behavior follows that theoretically predicted; however, the absolute values of $k_{\rm o}$ are approximately half that predicted for soft penetrable spheres.

A series of fractions of a hyperbranched polyester in chloroform solution have been examined with dilute-solution characterization methods, and ideas have been applied from classical two-parameter theory of polymer solutions. The viscosity contraction factor obtained by direct comparison with the data for an analogous linear polymer decreases with increasing molecular weight, that is, the hyperbranched polymer becomes relatively more compact at high molecular weight. A modification of the Stockmayer-Fixman extrapolation equation was used to extract a value for the unperturbed dimensions of the hyperbranched polymer, and this is twice that of the linear polymer. Evidently, there are stronger repulsions to internal rotation because of steric hindrance in the hyperbranched polymer. Characteristic radii of the polymer have the anticipated smaller scaling exponents with molecular weight as compared with those for linear polymers. These may be interpreted as a fractal dimension, the value of which suggests a flattened spherelike geometry for the branched polymer. The interpenetration function and the friction coefficient concentration factor both suggest that the polymer is not in particularly favorable solvent conditions and that the volume pervaded by a molecule is easily penetrated by another similar molecule, that is, the hyperbranched polymers are 'soft' structures in solution. Conversely, the values of $A_2 M_w/[\eta]$ increase with molecular weight suggesting that the polymer is hard and impenetrable.

The authors thank the Engineering and Physical Sciences Research Council for the provision of a maintenance grant to EDL that enabled this research.

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