Macromolecules **2004,** *37,* 3841−3849

Angular Dependence of Scattered Light from Hyperbranched Structures in a Good Solvent. A Fractal Approach

Walther Burchard[†]

Institute of Macromolecular Chemistry, Albert-Ludwig University of Freiburg, 79104 Freiburg

Received January 7, 2004; Revised Manuscript Received March 12, 2004

ABSTRACT: The neglect of excluded volume interaction in light scattering from randomly branched macromolecules leads to misinterpretation of the angular dependence. With a space correlation function of general fractal behavior $\gamma(r) = Ae^{-(r/\xi)}/(r/\xi)^{3-d}$ Feltoft et al. (*Phys. Rev. B* **1986**, *33*, 269) derived the corresponding particle scattering factor $P(qR_g)$ of the angular dependence of scattered light, where $q = (4\pi n_0/\lambda_0) \sin \theta/2$ is the value of the scattering vector, R_g is the radius of gyration, and ξ is a correlation length which is correlated to R_g. Complete agreement between theory and three sets of chemically different randomly branched clusters was obtained (*Macromolecules* **1997**, *30*, 2365) with a fractal dimension of $d = 1.76$ (renormalization group theory: $d_{RG} = 1.70$). In the present contribution, the Feltoft et al. approach is extended to hyperbranched and star-branched macromolecules. In contrast to randomly branched samples these structures are not selfsimilar objects. However, the angular dependence of these structures are well described by two different correlation lengths, ξ_{DB} and ξ_{lin}. The central part of the angular dependence is represented by a generalized Debye−Bueche space correlation function with correlation length ξ_{DB}, the asymptotic regime of large qR_g by that for polydisperse linear chains with correlation length ξ_{lin}. The theory is applied to partially degraded amylopectins. A considerably higher branching density was found from the experimental data with perturbed than unperturbed chains. The remaining deviations from literature data are attributed to the neglect of chain stiffness and heterogeneity in branching.

Introduction

The present paper deals with the influence of excluded volume interactions on the angular dependence of scattered light from large flexible macromolecules. The following treatment is based on physically well-supported space correlation functions of fractals, first considered by des Cloizeaux[1] and de Gennes.[2] The concept was further developed by Feltoft et al.[3] who added a cutoff function to take account of the finite size of macromolecules and clusters. The special choice of this cutoff function is physically not yet well-founded and may require further embellishment. Nonetheless, the results of the following treatment gives a more satisfying description of the scattering behavior from hyperbranched polymers than with the model of unperturbed conformations. The mathematical treatment is based on an analogous conclusion from the unperturbed behavior of hyerbranched samples. To make clear the procedure of this analogous treatment, a fairly expanded outline is given of the success with simpler structures than hyperbranched macromolecules in a good solvent.

On the basis of Debye's relationship[4] for the particle scattering factor of random coils of monodisperse and unperturbed linear chains Zimm[5] derived the well-known relationship for polydisperse chains[7,8] ($M_w/M_n = 2$) which is given by the equation[5]

$$P(u) = \frac{1}{1 + u^2/3} \tag{1}$$

where $u = qR_g$ and $P(u) = i(q)/i(q = 0)$ is the particle scattering factor. $R_g \equiv [\langle S^2\rangle_z)]^{1/2}$ is the root-mean-square radius of gyration (radius of gyration) in which the subscript indicates the *z*-average over the molar mass distribution. $q = (4\pi n_0/\lambda_0) \sin (\theta/2)$ is the magnitude of the scattering vector, with n_0 the solvent refractive index, λ_0 the wavelength of the light in a vacuum, and θ the scattering angle. Two comments may be appropriate.

(i) Both, the particle scattering factor $P(u)$ and the parameter $u = qR_g$ have no dimension, and eq 1 is a universal function of *u*. This implies that measurements from a special sample performed by different scattering techniques, e.g., light scattering (LS), small-angle neutron scattering (SANS), and small-angle X-ray scattering (SAXS), establish within experimental error one common curve.

(ii) The same result as given by eq 1 is also obtained for unperturbed randomly branched polymers, in which the distances between two segments follow Gaussian statistics.[9] This somewhat surprising result is caused by the fact that the effect of branching is exactly balanced by the influence of the exorbitant width in the molar mass distribution.[8,10] In contrast, branching in monodisperse samples causes a strong upturn in the Zimm plot, but a broad molar mass distribution causes a pronounced downturn.[11,12]

Despite the limitation of Gaussian statistics, most light-scattering experiments for linear synthetic polymers could successfully be described by eq 1, even for the samples in a good solvent. The reason for this observation is based on the comparatively small size of linear chains where mostly the radius of gyration is smaller than 100 nm such that $u = qR_g < 2$, and up to this *u* value eq 1 remains approximately valid for all types of particle architectures with weak deviation around $u = 2$. However, with branched materials, much larger molar masses and larger sizes can be realized extending to $u > 6$. In this range, the difference in architecture has a significant effect on the scattering curve. In a common plot of $P(u)$ against *u* the scattering

---

[†] E-mail: walther.burchard@makro.uni-freiburg.de.

10.1021/ma049950l CCC: $27.50

function from such large objects has already decayed to very low values, and this makes, in this plot, distinction of different architectures uncertain. On the other hand, even weak differences can be made apparent when the scattering data are represented in a plot of $u^2P(u)$ vs u, known as a Kratky plot. In this representation, the far u region is strongly amplified by factors of u^2.

The paper is organized as follows. Before the *perturbed* hyperbranched structures can be discussed, the success of Feltoft's et al. approach with perturbed linear and randomly branched samples is demonstrated. In another section, the strict correlation of the Debye–Bueche scattering with that from polydisperse linear chains is shown which establishes an essential requisite of the then following theoretical treatment. Both the behavior of scattering from linear chains and that of the Debye–Bueche scattering represent the two limits of a frame within which the hyperbranched structures are placed. After this preliminary outline, the actual extension to *perturbed* hyperbranched structures is given. Finally, the corresponding space correlation functions are derived, which instructively reveals the heterogeneity of these macromolecules.

Randomly Branched Samples with Excluded Volume Interaction

In an extensive work, Trappe et al.[13] collected scattering data from three different types of randomly branched macromolecules of various molar masses in a good solvent and presented the data in a Kratky plot. The three examples were (i) random tripolymerized polycyanates,[14] (ii) cross-linked polyester chains,[15] and (iii) end-linked three-arm polystyrene polymers.[16] The first two polymers were prepared in the melt and the last one was prepared in solution. One common curve was obtained with these chemically very different systems. Pronounced deviations from Zimm's eq 1 at large u values were observed. Instead of the predicted plateau value of about 3 at $u = 12$, a much higher value of 4.2 was found with no indication for a plateau.

Figure 1 shows the results for five polyester samples from the pregel state and from one sol fraction of a gel. For clarity, the data from the other samples are omitted. The universal curve for these different polymers clearly signifies self-similar behavior of randomly branched macromolecules.

A similar observation was made earlier with fractal aggregates, and this initiated Feltoft et al.[3] to use a space correlation function of the type

$$\gamma(r) = A\frac{\exp(-r/\xi)}{r^{3-d}} \tag{2}$$

with d the fractal dimension, ξ a correlation length, and a normalization constant A that will be given later in this paper. As already mentioned in the Introduction the $1/r^{3-d}$ dependence is physically well-founded, but the choice of a single exponential for the cutoff function is only a tentative assumption. Fourier transformation of eq 2 with regard to q gave the corresponding particle scattering factor[3]

$$P_{\text{fractal}}(u) = \frac{\sin[(d-1)\arctan(\xi q)]}{(d-1)(\xi q)(1+\xi^2q^2)^{(d-1)/2}} \tag{3}$$

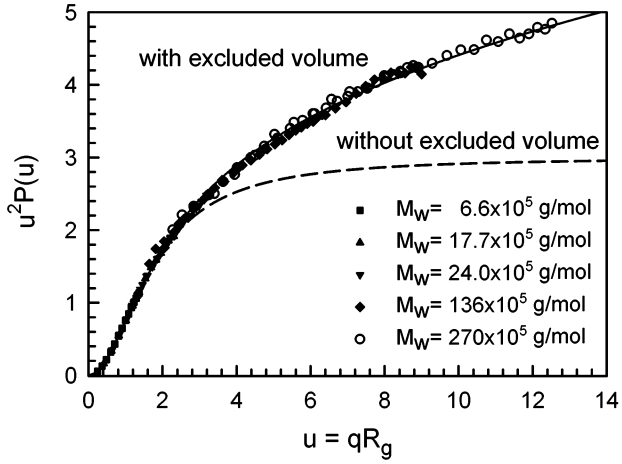

Figure 1. Scattering behavior of cross-linked polyester clusters in the Kratky representation.[15] Filled symbols: clusters from the pregel state. Open symbols: sol fraction sample from a gel. The dashed line represents the Zimm prediction for unperturbed polydisperse coils, and for randomly cross-linked chains in the unperturbed state. The solid line represents the fit of the data with the Feltoft et al.[3] function of eq 4 for objects with a fractal dimension of $d = 1.76$. (RG: $d = 1.70$.)

with

$$\xi^2 = \frac{2}{d(d+1)}{R_g}^2 \tag{4}$$

The solid curve in Figure 1 represents the fit by nonlinear regression with a fractal dimension of $d = 1.76 \pm 0.02$ which is slightly larger than $d = 1.70$ predicted from renormalization group (RG) theory for linear and randomly branched clusters in a good solvent. The good agreement between experiment and theoretical expectation supports a meaningful choice for the cutoff function in eq 2.

Debye–Bueche Scattering with Excluded Volume

Debye and Bueche[18] noticed that scattering curves from disordered systems are better described by a space correlation function of the type

$$\gamma(r)_{\text{DB}} = A_{\text{DB}}\exp(-r/\xi_{\text{DB}}) \tag{5}$$

rather than by eq 2. The Fourier transformation gave the well-known Debye–Bueche particle scattering factor[18]

$$P_{\text{DB}}(u) = (1 + u^2/6)^{-2} \tag{6}$$

with

$${\xi_{\text{DB}}}^2 = \frac{1}{6}{R_g}^2 \tag{7}$$

Equation 6 is a product of two equally structured functions of the type in eq 1. According to a general rule of Fourier transforms, the corresponding space correlation function of eq 5 had to arise from a convolution of two identical correlation functions, in the present case of the type as given by eq 2 for $d = 2$. The convolution behavior of eq 5 can be verified with eq 2 as the parental function but with different amplitude factors. Equation 2 was found to realistically describe the scattering behavior of polydisperse linear chains and of randomly branched macromolecules. A similar form can be expected from a convolution of the general space correlation function of eq 2 for fractal behavior of a Debye–Bueche type scattering *with* excluded volume interaction. To this end intuitively the function $1/(1 + u^2/6)$ in eq 6 solely has to be replaced by eq 3, which gives

$$P_{\mathrm{DB,fract}}(u) = \left[\frac{\sin[(d-1)\arctan(\xi_{\mathrm{DB}}q)]}{(d-1)(\xi_{\mathrm{DB}}q)(1+\xi_{\mathrm{DB}}{}^2q^2)^{(d-1)/2}}\right]^2 \qquad (8)$$

but with a different correlation length ξ_{DB} of

$$\xi_{\mathrm{DB}}{}^2 = \frac{1}{d(d+1)}R_{\mathrm{g}}{}^2 \qquad (9)$$

The original Debye–Bueche particle scattering factor is recovered for $d = 2$. From the rules of Fourier transformation, the square in eq 8 requests that this scattering behavior must originate from the convolution of two identical space correlation functions. It is likely, because of the fractional dimensionality, that the convolution of space correlation functions of the type of eq 2 has remained so far an unsolved problem.

Unperturbed Hyperbranched Macromolecules

The Debye–Bueche scattering function is often used as a simple fit function, but it also has a macromolecular basis. The same scattering function is obtained for very large hyperbranched flexible chain molecules.[19] Hyperbranched structures are formed with monomers which contain one so-called focal functional group A and at least two other functional groups B_1 and B_2.[8] Reaction can proceed only between the focal group A and one of the two B groups where B_1 may have a higher reactivity than B_2. For instance, B_1 could be a secondary hydroxyl group and B_2 a primary one. This stringent constraint permits excessive branching without gelation. This is understood when the extents of reaction α for the focal A group and β and γ for the B_1 and B_2 groups are considered. Necessarily one has

$$\beta + \gamma = \alpha \qquad (10)$$

but gelation only occurs when $1/(1 - \alpha) \to \infty$, which means full conversion of the focal end group.

The corresponding particle scattering factor for these generalized hyperbranched structures was derived previously by the present author[19] and is given by the equation

$$P_{\mathrm{hb}}(u) = \frac{1 + Cu^2/3}{[1 + (C+1)u^2/6]^2} \qquad (11)$$

in which $1/C$ is the number of branching points per macromolecule of number-average polymerization degree $\mathrm{DP_n} = 1/(1 - \alpha)$. (The exact relationship for C is given by eq 22; see also the Appendix). Incidentally, the same scattering curve was obtained for star-branched polymers[20] in which the arms have a length distribution of the most probable type. For these systems, one has $C = 1/f$, where f is the number of arms. The hyperbranched particle scattering factor encompasses two limits.

For $C = 1$, one obtains the particle scattering factor for polydisperse linear chains

$$P_{\mathrm{hb}}(u)_{C=1} = \frac{1}{1 + u^2/3} = P_{\mathrm{lin}}(u) \qquad (1')$$

and for $C = 0$, i.e., an infinite number of branching points, one finds the particle scattering factor for the Debye–Bueche structure[19b]

$$P_{\mathrm{hb}}(u)_{\mathrm{C}=0} = \frac{1}{[1 + u^2/6]^2} = P_{\mathrm{DB}}(u) \qquad (6')$$

Hypertbranched Macromolecules in a Good Solvent

The relationships for hyperbranched structures were derived on the basis of Gaussian statistics for every chain section between branching points. The corresponding fractal dimension of such chains is $d = 2$. With the Feltoft et al. approach, it was possible to extend the calculations for both limiting structures to fractal dimensions of $d < 2$. Therefore, it should be possible to include the generalized hyperbranched structures in this scheme.

The following conclusion is based on similarities in the mathematical structure of hyperbranched samples with linear and Debye–Bueche structures. For instance, the space correlation function for the unperturbed hyperbranched chains was found to be a linear combination of the correlation functions for polydisperse linear chains and Debye–Bueche structures (see below). It is sensible to presume that the same holds for the perturbed hyperbranched materials. Comparison of the numerator in eq 11 with Zimm's eq 1 reveals that the reciprocal of this numerator represents a scattering behavior of linear chain sections. Hence an extension to dimensions $d \neq 2$ may be possible by replacing the numerator by the inverse of eq 3 with a correlation length ξ_{lin}, and for the denominator the reciprocal Debye–Bueche type of particle scattering factor of eq 8. Then the generalized particle scattering factor is given by

$$P_{\mathrm{hb,fract}}(u) = P_{\mathrm{DB,fract}}(\xi_{\mathrm{b}}q)/P_{\mathrm{lin,fract}}(\xi_{\mathrm{lin}}q) \qquad (12)$$

where for $P_{\mathrm{DB,fract}}(\xi_{\mathrm{b}}q)$ eq 8 and for $\mathrm{P_{lin,fract}}(\xi_{\mathrm{lin}}q)$ eq 3 have to be inserted. With this approach one finds from the condition that the initial slope as a function of q^2 has to be $-R_{\mathrm{g}}{}^2/3$, which yields

$$\xi_{\mathrm{b}}{}^2 = \frac{C+1}{d(d+1)}R_{\mathrm{g}}{}^2 \quad \xi_{\mathrm{lin}}{}^2 = \frac{2C}{d(d+1)}R_{\mathrm{g}}{}^2 \qquad (13a,b)$$

and

$$u^2 = R_{\mathrm{g}}{}^2q^2 = [d(d+1)/2](2\xi_{\mathrm{b}}{}^2 - \xi_{\mathrm{lin}}{}^2)q^2 \qquad (14)$$

Equation 12 reduces to eq 11 for $d = 2$. Also, eqs 3 and 8 are recovered for $C = 1$ and $C = 0$, respectively. Figure 2 shows the result for various C parameters and $d = 1.7$ (good solvent: filled symbols) and $d = 2$ for the hyperbranched macromolecules in the unperturbed state (Θ solvent: open symbols).

Space- and Length-Correlation Functions

Recently it has become practice to consider the space-correlation function $\gamma(r)$ for interpretation rather than

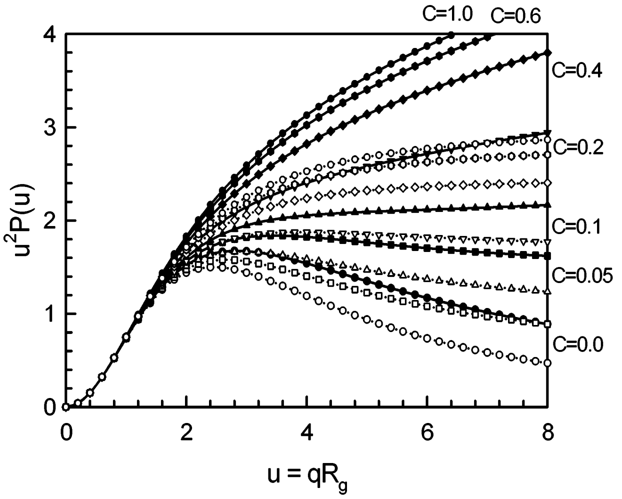

Figure 2. Kratky plots of the scattering behavior of hyperbranched macromolecules in the unperturbed states (open symbols) and with excluded volume interaction (filled symbols). A fractal dimension of $d = 1.7$ was assumed. The parameter $1/C$ is proportional to the number of branches per number-average degree of polymerization of the macromolecules. $C = 1$ represents the nonbranched linear chain, $C = 0$ an infinitely large hyperbranched macromolecule. The curve for $C = 0$ is identical with the Debye–Bueche approximation.

the particle scattering factor $P(q)$.[21] Probably this is favored because the particle scattering factor is expressed in an inverse space (q has the dimension of $1/r$) whereas the space correlation function is expressed in the familiar 3-dimensional space. The space correlation function is related to the segment density, but it does not directly represent the radial concentration profile in the particle.[22] Therefore, the space correlation functions are not self-explaining.

In this section, a comparison is made of the space correlation functions from various disordered hyperbranched structures. To this end, the normalization constants in $\gamma(r)$ have to be calculated. The particle scattering factors known in the literature were mostly derived within the frame of the Rayleigh–Gans theory from the double sum over all scattering elements in the particle. This double sum can be transformed into a singles integral, given by the relationship

$$P(q) = \frac{1}{N^2}\sum_j^N\sum_k^N\left\langle\frac{\sin(qr_{jk})}{qr_{jk}}\right\rangle = 4\pi\int_0^\infty \gamma(r)\frac{\sin(qr)}{qr}r^2\,\mathrm{d}r \qquad (15)$$

The angled brackets denote the average over the distance distribution $4\pi W(r_{jk})r^2\mathrm{d}r$ between two scattering elements j and k in the particle. Evidently, the function in angled brackets represents the Fourier transform of the distance distribution. Also the second part on the right side represents a Fourier transform, but now the discrete constitution of a macromolecular particle is disregarded, and the segment distributions is replaced by a continuous disordered matter. The inverted Fourier transform leads to the desired space correlation function as given by[23]

$$\gamma(r) = \frac{1}{2\pi^2}\int_0^\infty P(q)\frac{\sin(qr)}{qr}q^2\,\mathrm{d}q \qquad (16)$$

Although the definition of eq 16 is quite general, it may be worth emphasizing that the space correlation function has significant different behavior for disordered segment distributions than for monodisperse regular objects. In the former case the space correlation function strongly increases for decreasing distances with a power of $r^{-(3-d)}$ whereas for the regular particles a normalization of $\gamma(0) = 1$ can be made.[22] However, for the disordered systems the correlation function can be expressed in a scaled form (see below).

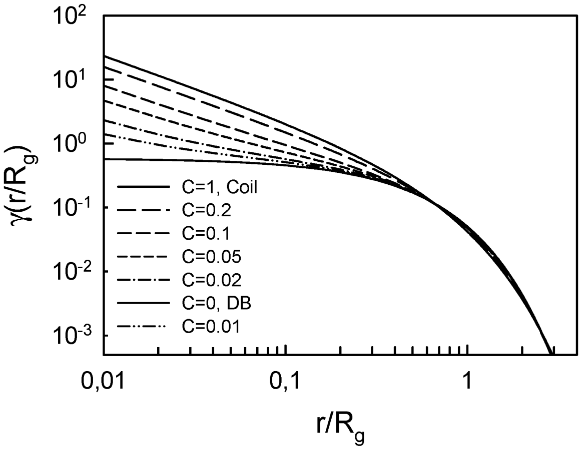

Figure 3. Scaled space correlation functions from *unperturbed* hyperbranched chains of different degrees of branching indicated by the parameter C. A value of $C = 1$ corresponds to the unperturbed linear chain and a value of $C = 0$ corresponds to the common Debye–Bueche scattering curve. $\gamma(r/R_g) = \gamma(r)R_g^3$

For all unperturbed structures given in this paper, the Fourier transform can be carried out analytically. For the *unperturbed* linear chains, the Debye–Bueche scattering and hyperbranched structures, the scaled space correlation functions $\gamma(r/R_g) \equiv \gamma(r)R_g^3$ are found to be

$$\gamma(r/R_g)_{\mathrm{linear}} = \frac{3^{3/2}}{4\pi}\frac{\exp(-(r/R_g)3^{1/2})}{(r/R_g)3^{1/2}} \qquad \text{linear random coil} \quad (17)$$

$$\gamma(r/R_G)_{\mathrm{DB}} = \frac{6^{3/2}}{8\pi}\exp(-(r/R_g)6^{1/2} \qquad \text{Debye–Bueche} \quad (18)$$

$$\gamma(r/R_G)_{\mathrm{hb}} = \frac{1}{8\pi}a^3\exp\left(-a\frac{r}{R_g}\right)\left[\frac{1-C}{1+C}+\frac{4C}{1+C}\frac{1}{ar/R_g}\right] \qquad \text{hyperbranched chains} \quad (19)$$

with

$$a = (6/(C+1))^{1/2} \qquad (19a)$$

Also the corresponding space correlation functions for linear chains of *fractal dimensions $d \neq 2$* could be solved analytically and are given by eq 20

$$\gamma(r/R_g) = \frac{1}{4\pi\Gamma(d)}b^3\exp\left(-\frac{br}{R_g}\right)\Big/\left[\frac{br}{R_g}\right]^{(3-d)} \qquad \text{chains with excluded volume} \quad (20)$$

with $b = (d(d+1)/2)^{1/2}$and $\Gamma(d)$ the γ function of the fractal dimension d.

For all hyperbranched structures with fractal dimensions $d \neq 2$, the inverse Fourier transformation had to be solved numerically. Figure 3 shows the scaled space correlation functions for the unperturbed hyperbranched

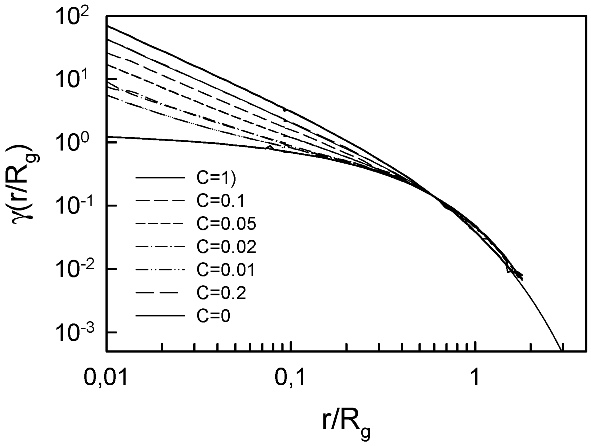

Figure 4. Scaled space correlation function of *perturbed* hyperbranched macromolecules with fractal behavior of subchains. A fractal dimension of $d = 1.7$ was chosen. The effect of excluded volume becomes noticeable only in the regime of short chain sections, corresponding to the asymptotic region of large scattering angles.

chains and Figure 4 the perturbed correlation functions for the same structures *with excluded volume* interaction.

The space correlation function of the hyperbranched macromolecules displays an interestingly heterogeneous structure. The *global part*, or core, is well described by the space correlation of the *Debye–Bueche* suggestion $[\sim\exp(-a(r/R_g)]$ but the *short length domain* is well represented by the behavior of *fractal linear chains* $[\sim\exp(-a(r/R_g)/a(r/R_g)]$ with $a = [6/(C+1)]^{1/2}$ where the corresponding global and linear contributions are controlled by the number of branches in the particle. The same behavior as given for the hyperbranched structures is obtained for star branched macromolecules, but with $C = 1/f$.[20]

In principle, the correlation function for the hyperbranched scattering with excluded volume should be a linear combination of the corresponding correlation functions of the linear chain and the Debye–Bueche scattering, in a similar manner as was given for the unperturbed dimensions. The problem arises from the fact that the Debye–Bueche correlation function with excluded volume is not yet known to us. The common convolution of the linear chain type correlation function in the Euclidian space leads to a incorrect result.

The *length* correlation function[21] is defined by

$$p(r/R_g) \equiv 4\pi(r/R_g)^2\gamma(r/R_g) \qquad (21)$$

This function is well-defined and displays no singularity at $r = 0$. Figure 5 shows the behavior for unperturbed linear chains and Debye–Bueche structures in the unperturbed (open symbols) and perturbed (filled symbols) states. The length correlation functions pass through a maximum but on the whole the change due to excluded volume interactions is small in the scaled representation. The effect becomes more marked if the length correlation function is expressed in real distances.

Comparison with Experiment

Hyperbranched structures have been prepared in the meantime with various monomers which possess one focal group A and two equally reactive B groups.[24] Much lower molar mass than expected was obtained, probably because of ring formation or other side reactions. The A end group could have reacted *intra*molecularly with a B group of an already formed macromolecule by which the only A group in that particle disappears. It has not yet been possible to obtain large hyperbranched macromolecules with radii of gyration in the range of the wavelength needed for light scattering. SANS and SAXS could be applied to probe the structure in the large qR_g regime, but interpretations have to be made with caution, because ring formation changes the internal segment density, and this is correlated to the angular dependence. Also, because of the small size, excluded volume interactions may be weak.

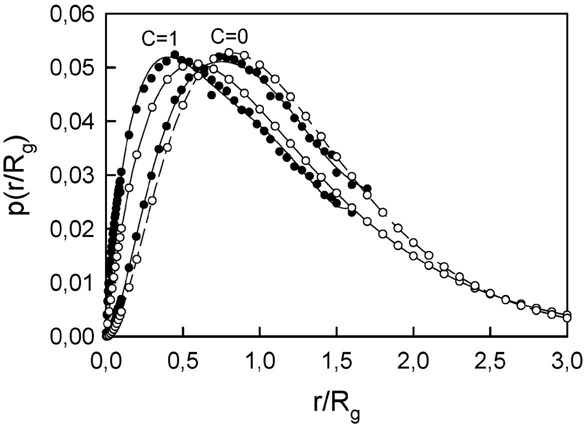

Figure 5. Length correlation function $p(r/R_g) = 4\pi\gamma(r/R_g)(r/R_g)^2$ for linear chains ($C = 1$) and hyperbranched chains in the limit of infinite number of branches ($C = 0$). Open symbols: unperturbed chains. Filled symbols: chains with excluded volume imteraction ($d = 1.7$).

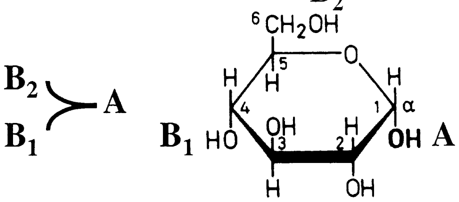

Figure 6. α-Glucose and the corresponding graph model. In amylopectin, the reducing end group establishes a focal-end group A, which due to the specifity of enzymes only can react with the hydroxyl groups (B_1) and (B_2) in the C4 and C6 position of the ring. The reaction with B_1 is about 25 times more frequent than with the B2 group. If both B groups have reacted, a branching point is created.

Nature, however, presents some interesting examples with amylopectin and probably also with some other polysaccharides, which contain a reducing end group as the focal functionality. The branched structure is built up of glucose in which the reducing end group establishes the focal group A. By the action of specific enzymes glycosidic bonds are formed between the secondary OH group in the C_4 position and the focal group in C_1 and to a much less extent also between the primary OH group in the C_6 position and the focal group in C_1.[25] See Figure 6.

If both nonreducing end groups have reacted, a branching point is obtained. In amylopectin only 4–4.5% of all monomer units in the macromolecule are branching units. A simple statistical model, suggested by Meyer and Bernfeld,[26] is given on the basis of Figure 6 together with the chemical structure of the glucose, in which the focal group A and the two other groups B and

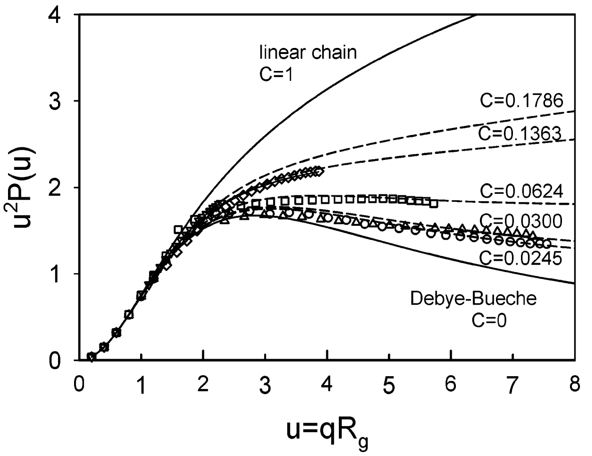

Figure 7. Scattering curves from fife specifically degraded amylopectins[34] (symbols). The dashed lines are fit-curves, assuming good solvent behavior. A fractal dimension of $d = 1.7$ was assumed for the linear chains, connecting branching points, and for the dangling chains in the corona. The two solid lines refer to linear chains and to Debye−Bueche scattering.

Table 1. Molar Mass M_w, Radius of Gyration R_g, Weight Average Degree of Polymerization DP_w and Branching Parameters C_0 and C for Unperturbed and Perturbed Hyperbranched Samples of Degraded Amylopectin, Where the Branching Probability is $p(1 - p)$ and Multiplication with the DP_w Gives the Number of Branches in the Particle

$M_w \times 10^{-6}$, g/mol	R_g, nm	$DP_w \times 10^{-3}$	C_0	$1/C_0$	C	$1/C$	$p(1 - p) \times 10^4$
5.1	71	31.5	0.5	2.00	0.1786	5.59	4.97
13.9	120	85.8	0.33	3.03	0.1363	7.33	3.13
50	180	308.6	0.215	4.65	0.0624	16.0	4.16
97	227	598.8	0.155	6.45	0.0300	33.3	9.27
104	229	642.0	0.115	8.69	0.0245	40.7	12.86

C are assigned to the OH− in the C_4 and the $-CH_2OH$ in the C_6 positions. The statistical theory of the Meyer−Bernfeld model was first treated by Flory[8] with the simplification that the two OH groups in C_4 and C_6 position have equal reactivity, generalized by Erlander and French[27] and finally extended by the present author[19] to static light scattering in Θ-solvents, i.e., the unperturbed radius of gyration and the corresponding particle scattering factor (see eq 11).

However, the biosynthesis of amylopectin is more complex than presented by Figure 6 on the basis of a random statistical point of view. By a not yet fully explored mechanism of the biosynthesis,[28] the starch macromolecules are packed in semicrystalline granules in the range of several micrometers. The required dissolution of the native starch is difficult and requires a rather harsh treatment which may cause an uncontrolled degradation. However, by a special treatment, first employed by Fox and Robyt,[33] a series of well-defined and easily dissoluble starch fragments could be prepared,[34] which should reflect the hyperbranched properties. Figure 7 shows the Kratky plots from five samples whose dimensions were large enough to exceed values of $u > 2$. The number at the various curves represent the values of the branching parameter C which were found by nonlinear fits of the experimental data with eq 12.

The data for the molar mass M_w, the radius of gyration R_g and the branching parameter C, with and without excluded volume, are listed in Table 1.

According to the theory of hyperbranched macromolecules the parameter C is given for particles of $DP_w \gg 1$ by the equation[19]

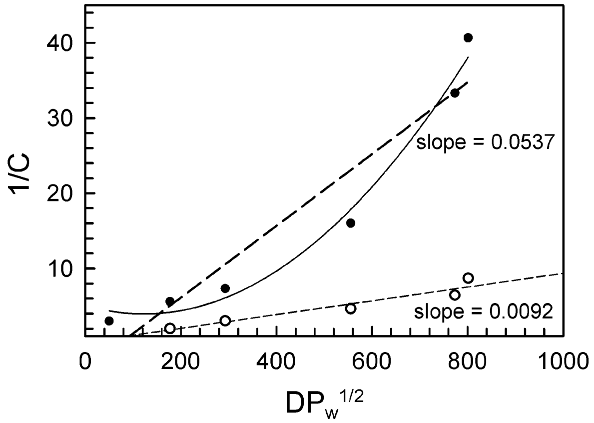

Figure 8. Dependence of the reciprocal branching parameter $1/C$ on the root of the weight-average degree of polymerization. The open symbols were obtained for the macromolecules in the unperturbed state, while the filled symbols resulted from fits with excluded volume interaction ($d = 1.7$).

$$1/C \cong [2p(1 - p)DP_w]^{1/2} \tag{22}$$

in which $p(1 - p)$ is the probability of finding an anhydroglucose unit in the macromolecule that acts as a branching point, i.e., with α(1,4) and α(1,6) linkages. Thus, the number of branching points per weight-average degree of polymerization is

$$N_b = p(1 - p)DP_w = 1/(2C^2) \tag{23}$$

The number of branch points is a covalently fixed structure parameter and remained unchanged when the macromoleule is transferred from a theta into a good solvent. The branching probability can be estimated from the slope of $1/C$ against $DP_w^{1/2}$. The result is shown in Figure 8 for the data obtained with excluded volume interaction (filled symbols and long-dashed line), and these are compared with those for unperturbed chains (open symbols, short-dashed line). The scatter of the data is large, and the application of a linear regression fit may be doubtful (the full line is a second-order regression line through the experimental points). Still the average slope is considerably larger with excluded volume interaction than without it.

Under the assumption that the branching density is not affected by the degradation, the corresponding degrees of branching are

$$[p(1 - p)]_{\text{excl. vol}} = 1.44 \times 10^{-3} \quad \text{with excluded volume}$$

$$[p(1 - p)]_0 = 4.23 \times 10^{-5} \quad \text{no excluded volume}$$

When the excluded volume interaction is taken into account, a considerably larger branching probability by a factor of 34 is obtained than that with a fit without excluded volume. Still this value remained about 28 times smaller than the expected value of $p(1 - p) \approx 4 \times 10^{-2}$. This obtained crude average would mean that the degradation of amylopectin in the semicrystalline grain is actually a debranching process. The curvature in Figure 8 and the actual data points seem to support this. Clearly more experimental data are required and results from samples of lower $DP_w < 4000$, ($M_w < 650\,000$ g/mol). Low molar mass samples of $M_w = 33\,000$

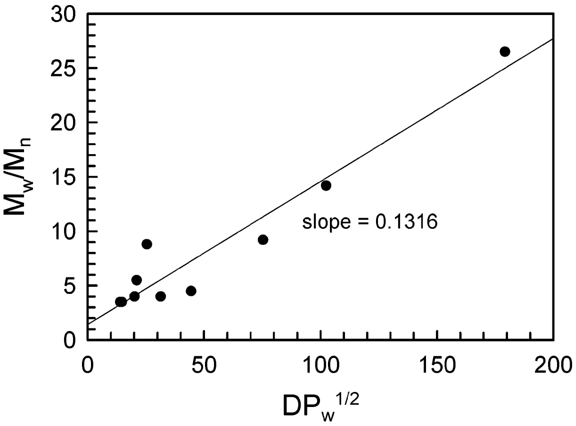

Figure 9. Dependence of the molecular polydispersity on the root of the weight-average degree of polymerization. The symbols represent experimental data, and the line represents the linear regression.

g/mol and higher have been prepared with radii of gyration of about 3 nm. For a check of the angular dependence at large qR_g values, the smaller wavelength of cold neutrons has to be used.

The hyperbranching theory can be tested by another method in which the excluded volume interaction has no influence. It has been possible to determine the number-average molar mass by titration of the reducing end group[34a] (the focal end group). Together with the weight-average molar mass that was determined by light scattering the polydispersity index M_w/M_n could be determined, and this value is again related to the branching probability by (see the Appendix)

$$M_w/M_n \cong [2p(1-p)]^{1/2}\mathrm{DP_w}^{1/2} \tag{24}$$

Figure 9 shows the plot of M_w/M_n against $\mathrm{DP_w}^{1/2}$. From the slope of 0.131, the branching probability is found to be

$$p(1-p)_{M_w/M_n} = 8.66 \times 10^{-3}$$

This value is still 5 times smaller than the 4−4.5% branching that was estimated from the analysis of fully degraded permethylated samples.[25,35,36]

The prepared samples have a considerably narrower molar mass distribution than predicted by the statistics for hyperbranching.[19,27] Evidently the branching process in the biosynthesis of amylopectin does not strictly follow a random-statistical mechanism but is controlled by the cooperative action of various enzymes which led to branching heterogeneity, but possibly also to a certain regularity, for instance in the distribution of the chains in the branched macromolecule.

At this point some additional comments on the supramolecule structure of native starches have to be made. As already mentioned, the starch molecules, amylopectin and amylose, are densely packed in a granule which is built up of alternating semicrystalline and amorphous shells. The semicrystalline shell in turn are separated by a thin amorphous layer where the distance between two such amorphous layers is about 9 nm for all types of starches.[28−32] It is now well understood that the crystalline sections of the layer are established by amylopectin chains which are in a double helix conformation, and the thin amorphous layer is supposed to contain the branching areas which apparently do not fit the crystal structure.[30−32] The linear amylose is supposed to be in the amorphous shells and seems to perturb the crystalline structure.

When an acid degradation is made in methanol, the crystalline structure is not broken up, and the degradation takes place predominantly in the noncrystalline layer where the branching points are supposedly being located. No significant change in the chain length of the crystalline branches will occur. Thus, we could expect that the degradation in this medium cuts out starch fragments from the native amylopectin molecules, and these fragments may still keep the essential features of amylopectin. Basically, this picture turned out to be qualitatively correct. A full agreement with the simple statistical hyperbranching model cannot be expected, because of some regularities in the amylopectin molecule. Application of careful degradation experiments in a defined sequence of specific enzymes made it clear that the branching points are clustered and not statistically distributed as given in the hyperbranching model. This fact may be one reason for the failure of finding the expected high branching density. Another point is the neglect of chain stiffness, which certainly is present in the chains.

Concluding Remarks

Clearly the complex molecular architecture of amylopectin and the embedding of these macromolecules in a fairly ordered granule renders this material not as suitable a prototype for a test of the present approach. Actually, it only was used as no chemically synthesized hyperbranched samples of the required size were available. Although the employed model is much too simple, it can be stated that the experimental curves are quantitatively better described when excluded volume interactions are taken into account. Probably the reported heterogeneity in branching[25,27−32] is only one reason for the low degree of branching found by the statistical hyperbranching model. More important for the failure of a quantitative agreement is the neglect of chain stiffness which certainly is present. From experience with stiff star-branched macromolecules,[37] we know already that the asymptotic part in the Kratky plot is moved toward higher values,[38] which would feign a smaller number of arms at a lower branching density. The introduction of chain stiffness into the theory of hyperbranching is difficult but may be possible. Some ideas are already available how to handle this problem and attempts are in progress. Figure 16 in ref 38 demonstrates a stronger increase of the asymptote at large u values, which is more pronounced than by the excluded volume interaction.[39] Monte Carlo simulation by Huber et al.[40] and Molina et al.[41] confirmed this conclusion. Therefore, a higher branching density, closer to values of about 4%, can be expected from an analysis of hyperbranched polymers with semiflexible linear chain segments.

A somewhat similar approach was developed earlier by Dozier et al.[42] for a description of the SANS behavior of monodisperse 12-arm and 18-arm star molecules.In this approach the central part of the molecules was fitted by the common Guinier approximation (which has no relation to a model) and the linear chain behavior by the Feltoft equation, eq 3. Indeed the Guinier approximation was found in a check[43] to be an excellent fit if the number of arms was larger than 5. The application of Feltoft's equation to the linear chains remains, however, doubtful, because the use of the corresponding space correlation function is based on disordered systems and includes poydisperse chains of the most probable distribution. The correlation function of monodisperse linear chains is even for the unperturbed chains more complex, and an analytic extension equivalent to the Feltoft et al. approach had not yet been made. In the present paper, the Debye−Bueche space correlation function is a direct consequence of the polydisperse hyperbranching, at least for the unperturbed structures. The extension to perturbed chains admittedly is a semiempirical attempt, but it has the advantage that the linear chain and the limiting case of infinitely large hyperbranched objects are correctly described.

As a final remark, it should be emphasized that fractal behavior is only valid in the intermediate regime between the radius of gyration and the bond length. Furthermore, as was outlined by Daoud and Cotton[44] with star-branched macromolecules, there can be an overcrowding effect of segments in the core of the macromolecule which causes a stretching out of the branches combined with a complete screening of the excluded volume interaction. However, overcrowding and strong excluded volume screening will be small with hyperbranched chains if the branching density is low.

Acknowledgment. This paper is affectionately dedicated to Professor Walter H. Stockmayer on the occasion of his 90th birthday. Professor Stockmayer had been the silent teacher for me many years before I met him personally. His early papers in the years after the war were absorbed by me with delight as a desirable way to quantitative polymer science. His generosity in offering help in the difficult period after the war will never been forgotten and is greatly acknowledged.

Appendix

Some molecular parameters of hyperbranched macromolecules are given as follows.

Extents of reaction:

$$\alpha \quad \text{for the focal end group A}$$
$$\beta = \alpha(1-p) \quad \text{for the functional group } B_1$$
$$\gamma = \alpha p \quad \text{for the functional group } B_2$$

Constraint:

$$\beta + \gamma = \alpha$$
$$DP_n = M_n/162, \quad DP_w = M_w/162$$

Molar mass averages:

$$M_n = \frac{162}{1-\alpha} \rightarrow 162\frac{[1+2p(1-p)DP_w]^{1/2}-1}{2p(1-p)}$$

$$M_w = 162\frac{1-\beta^2-\gamma^2}{(1-\alpha)^2} \rightarrow 162\frac{2p(1-p)^2}{(1-\alpha)^2}$$

$$\frac{M_w}{M_n} = 1 + [1+2p(1-p)DP_w]^{1/2}$$

Branching parameter:

$$\frac{1}{C} = \frac{[1+2p(1-p)DP_w]^{1/2}}{1-2p(1-p)} \rightarrow [2p(1-p)DP_w]^{1/2}$$

The arrows indicate asymptotic behavior when $\alpha \approx 1$, i.e., $DP_n \gg 100$ and $DP_w \gg 1000$.

References and Notes

(1) Des Cloizeaux, J. *Phys. Rev.* **1974**, *A10*, 1665.
(2) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(3) Feltoft, F.; Kjems, J. K.; Sinha, S. K. *Phys. Rev. B* **1985**, *33*, 269.
(4) Debye, P. In *Light Scattering from Polymer Solutions*; McIntyre, D., Gornick, F., Eds.; Gordon & Breach: New York, 1964; p 139.
(5) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093, 1099.
(6) Schulz, G. V. *Z. Phys. Chem.* **1939**, *B43*, 25.
(7) Flory, P. J. (a) *J. Am. Chem. Soc.* **1942**, *64*, 2205. (b) *J. Chem. Phys.* **1944**, *12*, 426.
(8) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(9) Kajiwara, K.; Burchard, W.; Gordon, M. *Br. Polym. J.* **1970**, *2*, 110.
(10) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45; **1944**, *12*, 125.
(11) Burchard, W. *Adv. Polym. Sci.* **1983**, *48*, 1, pp.53.
(12) Kajiwara, K. *Polymer* **1971**, *12*, 57.
(13) Trappe, V.; Bauer, J.; Weissmüller, M.; Burchard, W. *Macromolecules* **1997**, *30*, 2365.
(14) Bauer, M.; Bauer, J. In *The Chemistry and Technology of Cyanate Ester Resins;* Hamerton, J., Ed.; Chapman & Hall: Glasgow, Scotland, 1994.
(15) (a) Trappe, V.; Burchard, W.; Steinmann, B. *Macromolecules* **1991**, *24*, 4738. (b) *Makromol. Chem., Macromol. Symp.* **1991**, *45*, 63. (c) *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *36*, 1.
(16) Weissmüller, M.; Burchard, W. (a) *Polym. Int.* **1997**, *44*, 380. (b) *Acta Polym.* **1997**, *48*, 571. (c) *Macromol. Chem. Phys.* **1999**, *200*, 541.
(17) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York 1987.
(18) Debye, P.; Bueche, A. M. *J. Appl. Phys.* **1949**, *20*, 518.
(19) Burchard, W. *Macromolecules* **1972**, *5*, 604. (b) Burchard, W. *Macromolecules* **1977**, *10*, 919.
(20) Burchard, W. *Macromolecules* **1974**, *7*, 841.
(21) Glatter, O. In *Small-Angle X-ray Scattering*; Glatter, O., Kratky, O., Eds.; Academic Press: London, 1982; Chapter 5.
(22) Guinier, A.; Fournet, G. *Small Angle Scattering of X-rays*; Wiley: New York, 1955.
(23) Porod, G. In *Small-Angle X-ray Scattering*, Glatter, O., Kratky, O., Eds.; Academic Press: London, 1982; Chapter 2.
(24) Hult, A.; Johanssen, M.; Malmström, E. *Adv. Polym.. Sci.* **1999**, *143*, 1.
(25) Guilbot, A.; Mercier, C. Starch. In *The Polysaccharides*; Aspinall, G. O., Ed.; Academic Press: Orlando, FL, and San Diego, CA, 1985; Vol. 3.
(26) Meyer, K. H.; Bernfeld, P. *Helv. Chim. Acta* **1940**, *23*, 865.
(27) Erlander, S.; French, D. *J. Polym. Sci.* **1956**, *20*, 7.
(28) Smith, A. M. *Biomacromolecules* **2001**, *2*. 335.
(29) Robin, J. P.; Mercier, C.; Duprat, F.; Charboniere, R.; Guilbot, A. *Starch/Stärke* **1975**, *27*, 36.
(30) Jenkins, P. J.; Cameron, R. E.; Donald, A. M.; Bran, W.; Derbyshire, G. E.; Mant, G. R.; Ryan, A. *J. Polym. Sci., Phys Ed.* **1994**, *32*, 1579.
(31) Jenkins, P. J.; Donald, A. M. *Int. J. Biol. Macromol.* **1995**, *17*, 315.
(32) Damaschun, G. In Report to the project of "Amyloseverbund" supported by the DFG, 1993.
(33) Fox, J. A.; Robyt, J. F. *Carbohydr. Res.* **1992**, *227*, 166.
(34) Galinsky, G.; Burchard, W. *Macromolecules* **1995**, *28*, 2363. (b) Galinsky, G.; Burchard, W. *Macromolecules* **1996**, *29*, 1498. (c) Galinsky, G.; Burchard, W. *Macromolecules* **1997**, *30*, 4445. (d) Galinsky, G.; Burchard, W. *Macromolecules* **1997**, *30*, 6966.
(35) Whistler, R. L.; Daniel, J. R. Molecular Structure of Starch. In *Starch: Chemistry and Technology*; Whistler, R. L., BeMiller, J. M., Paschall, E. F., Eds.; Academic Press: Orlando, FL, and San Diego, CA, 1984, Chapter 6.

(36) Banks, W.; Greenwood, C. T. *Starch and its Components*; Edinburgh University Press: Edinburgh, Scotland, 1975.
(37) Huber, K.; Burchard, W. *Macromolecules* **1989**, *22*, 3332.
(38) Freire, J. J. Conformational Properties of Branched Polymers: Theory and Simulations. *Adv. Polym. Sci.* **1999**, *143*, 35.
(39) (a) Ganazzoli, F.; La Ferly, R.; Terragoni, G. *Macromolecules* **2000**, *33*, 6611. (b) Ganazzoli, F.; La Ferla, R.; Raffaini, G. *Macromolecules* **2001**, *34*, 4222. (c) Ganazzoli, F. *Macromol. Symp.* **2002**, *190*, 55.
(40) Huber, K.; Burchard, W.; Bantle, S.; Fetters, L. J. *Polymer* **1987**, *28*, 19990, 1997.
(41) Molina, L. A.; Rey, A.; Freire, J. J.*Comput. Theor. Polym. Sci.* **1998**, *17*, 243.
(42) Dozier, W. D.; Huang, J. S.; Fetters, L. J. *Macromolecules* **1991**, *24*, 2810.
(43) Savin, G.; Burchard, W. *Macromolecules* **2004**, *37*, in press.
(44) Daoud, M.; Cotton, J. P. *J. Phys. (Paris)* **1982**, *43*, 531.

MA049950L