

Structure Factor for Starburst Dendrimers

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SYNOPSIS

Advances in polymer synthesis have made possible the polymerization of "starburst dendrimer" gels which are grown from a central initiator core through controlled branching reactions with a constant multiplication of the number of monomeric blocks from one generation to the next. The structure factor for such dendrimers is calculated using Gaussian monomer-monomer interactions. The results are somewhat lengthy but analytical forms are obtained. © 1992 John Wiley & Sons, Inc.

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INTRODUCTION

Advances in polymer synthesis are making possible the polymerization of complicated chain architectures. Synthesis of highly regular structures such as stars, combs, dendrimers, etc. are now possible. "Starburst dendrimers"^{1,2} (also referred to as "cauliflower" polymers) are regular polymer gels that grow through multifunctional polymerization reactions starting from an initiator core and branching outward with a multiplication of the number of monomeric blocks from one generation to the next (Fig. 1). These dendrimers have unique structural and topological features and may develop into important polymer materials. Advances in the interpretation of small-angle neutron-scattering (SANS) data, based on the random-phase approximation model or on the Ornstein-Zernicke type of approach have also made possible the characterization of rather complicated polymer systems provided that the "bare" interaction (single macromolecule) structure factors are available. In anticipation of the availability of SANS measurements on dendrimer gels in solutions or mixed with other compatible polymers, the single macromolecule structure factor for such gels is calculated here. A similar calculation was performed by Burchard et al.³ using the "cascade" theory. The present calculations are based on

a direct approach and leave the functionality as an arbitrary parameter.

CALCULATION OF THE VARIOUS STRUCTURE FACTORS

A simple parametrization of the problem follows: the dendrimer is regular and formed of N_b branches. Each branch is formed of N generations of monomeric blocks. The number of blocks is multiplied by a factor f in going from one generation to the next. Note that the "functionality" parameter is defined, here, as $f + 1$. Each block is composed of n monomers forming Gaussian links with segment length b .

Correlations between any two different blocks separated by m blocks are given as:

$$[F(\alpha, n)]^2 \exp[-\alpha n m] \quad (1)$$

in terms of the form factor:

$$\begin{aligned} F[\alpha, n] &= \sum_i^n \exp[-\alpha i] \\ &= [1 - \exp(-\alpha n)] / [\exp(\alpha) - 1] \quad (2) \end{aligned}$$

where $\alpha = Q^2 b^2 / 6$ has been defined as the dimensionless scattering variable. Note that in the limit of $\alpha \ll 1$,

DENDRIMER POLYMER GEL

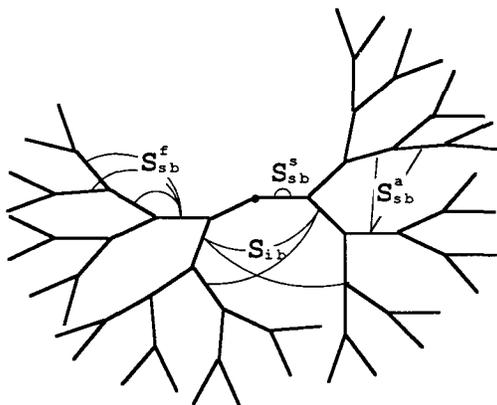


Figure 1. Schematic two-dimensional representation of a dendrimer polymer gel.

$$F[\alpha, n] = [1 - \exp(-\alpha n)]/\alpha. \quad (3)$$

When the correlations are between monomers that belong to the same block, then, the "finite-chain" structure factor for Gaussian chain portions is used:

$$P[\alpha, n] = \sum_{i,j}^n \exp[-\alpha|i-j|] \quad (4)$$

and is calculated as:

$$P[\alpha, n] = n + 2n \{1 - [1 - \exp(-\alpha n)]/[n(1 - \exp(-\alpha))]\} / (\exp(\alpha) - 1). \quad (5)$$

Here also, note that in the limit $\alpha \ll 1$, $n \ll 1$ with $\alpha n = Q^2 R_g^2$ remaining finite, $P[\alpha, n]$ becomes the well known Debye function (normalized to n^2):

$$D[\alpha n] = 2n^2 \{1 - [1 - \exp(-\alpha n)]/n\alpha\} / (\alpha n)^2. \quad (6)$$

The calculations of the various structure factors for a dendrimer gel are rather straightforward, but somewhat tedious. There are four main contributions to these correlations: (1) one intrabranched self-correlation part S_{sb}^s , (2) one intrabranched cross-correlation part S_{sb}^f , between blocks that originate from the same stem, (3) one intrabranched cross-correlation part S_{sb}^a , between blocks that originate from different stems, and (4) one interbranch correlations part S_{ib} . These various correlations are sketched in Figure 1.

The intrabranched self-correlation term in the structure factor involves monomer-monomer correlations within the same block. Since there are $f^{(k-1)}$ blocks in generation k , the total number of blocks per branch is:

$$\sum_{k=1}^N f^{k-1} = (f^N - 1)/(f - 1) \quad (7)$$

therefore giving:

$$S_{sb}^s(Q) = [(f^N - 1)/(f - 1)]P(\alpha, n). \quad (8)$$

The intrabranched cross-correlations between blocks that originate at the same stem involve summations over blocks in generations k and l , respectively, and form factors internal to each block:

$$S_{sb}^f(Q) = 2[F(\alpha, n)]^2 \sum_{k=1}^N f^{k-1} \sum_{l=k+1}^N f^{l-k} \times \exp[-\alpha n(l - k - 1)]. \quad (9)$$

These summations can be easily performed to give an analytical expression:

$$S_{sb}^f(Q) = 2\{[F(\alpha, n)]^2/[f \exp(-\alpha n) - 1]\} \times \{f^N \exp(-\alpha n N)[\exp(\alpha n N) - \exp(\alpha n)] / [\exp(\alpha n) - 1] - (f^N - f)/(f - 1)\}. \quad (10)$$

Similarly, for the intrabranched cross-correlations between blocks that originate from different stems, three summations are involved: the previous two (over k and l) and a third summation over the number of stem points (m) that have to be crossed in order to join the two blocks under consideration:

$$S_{sb}^a(Q) = 2[F(\alpha, n)]^2 \sum_{k=2}^N f^{k-1} \sum_{m=1,2}^{2k-3} \times (f - 1) f^{(m-1)/2} \exp[-\alpha n(m - 1)] \times \left\{1 + 2 \sum_{l=k+1}^N f^{l-k} \exp[-\alpha n(l - k)]\right\}. \quad (11)$$

In other words, in going from block k to block l , one has to meet m stems with $(f - 1)f^{(m-1)/2}$ as the number of possibilities. The summations can be performed to give:

$$S_{sb}^a(Q) = 2[F(\alpha, n)]^2 \{ (f-1) / [f \exp(-2\alpha n) - 1] \} \{ A(Q) + B(Q) \}$$

$$A(Q) = [f^{2N} \exp(-2\alpha n N) - f^2 \exp(-2\alpha n)] / [f^2 \exp(-2\alpha n) - 1] - (f^N - f) / (f - 1)$$

$$B(Q) = 2 \{ f^N \exp(-\alpha n N) [f^N \exp(-\alpha n N) - f \exp(-\alpha n)] / [f \exp(-\alpha n) - 1] - f \exp(-\alpha n) \} \times [f^{2N} \exp(-2\alpha n N) - f^2 \exp(-2\alpha n)] / [f^2 \exp(-2\alpha n) - 1] - f^N \exp(-\alpha n N) \times [\exp(\alpha n N) - \exp(\alpha n)] / [\exp(\alpha n) - 1] + f \exp(-\alpha n) (f^N - f) / (f - 1) \} / [f \exp(-\alpha n) - 1]. \quad (12)$$

Note that this term is proportional to $(f - 1)$ and goes to zero for star-branched polymers ($f = 1$). Finally, the interbranch correlations are:

$$S_{ib}(Q) = [F(\alpha, n)]^2 \sum_{k=1}^N f^{k-1} \sum_{l=1}^N f^{l-1} \times \exp[-\alpha n(l + k - 2)] \quad (13)$$

and are summed up to give:

$$S_{ib}(Q) = [F(\alpha, n)]^2 [f^N \exp(-\alpha n N) - 1]^2 / [f \exp(-\alpha n) - 1]^2. \quad (14)$$

The total structure factor is the sum of all of these partial structure factors:

$$S(Q) = N_b [S_{sb}^s(Q) + S_{sb}^f(Q) + S_{sb}^a(Q)] + N_b(N_b - 1)S_{ib}(Q). \quad (15)$$

In order to obtain a structure factor which is normalized to unity, one has to divide $S(Q)$ by N_T^2 where $N_T = [nN_b(f^N - 1)/(f - 1)]$ is the total number of monomers in the gel.

DISCUSSION

Figure 2 shows the behavior of $S(Q)$ for increasing number of generations N when all other parameters are fixed. As expected, the radius of gyration increases with N . Varying the number of branches has a similar effect. the variation of f , on the other hand, has a smaller effect. Burchard et al.³ consid-

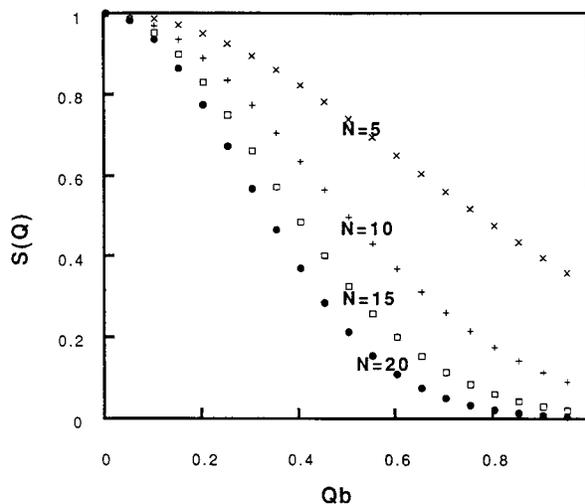


Figure 2. Variation of the structure factor $S(Q)$ with the dimensionless variable Qb for a dendrimer polymer gel with $N_b = 3$, $f = 2$, $n = 1$, and with N varying from 5 to 20.

ered the case where the number of generations is varied while keeping the total number of monomers N_T constant. A similar situation is considered in Figure 3 which corresponds to the case $N_T = 10,000$ (kept constant), $N_b = 3$ and $b = 5$. The relative radius of gyration (R_g/b) is obtained by performing Guinier fits ($\text{Log}[S(Q)]$ vs Q^2) and plotted in Figure 3 for increasing number of generations. Two cases are considered: $f = 2$ (trifunctional branching) and $f = 3$ (tetrafunctional branching). Even in this simple-minded Gaussian model, the starburst dendrimer is seen to become more and more compact when the number of generations and the functionality are increased.

The calculations presented here are based on the assumptions of Gaussian interactions between monomers. In order to account for excluded volume effects (swelling) or chain collapse (shrinking) effects, it is customary to use an excluded volume parameter ν in an ad hoc manner, i.e., by redefining $\alpha = Q^2 b^2 / (2\nu + 1)(2\nu + 2)$ and replacing nN by $(nN)^{2\nu}$. This procedure has no justification other than it can mimic swelling and is often used along with the Debye function (with a swollen radius of gyration) for linear chains. Assuming an excluded volume parameter from the outset by replacing $|i - j|$ by $|i - j|^{2\nu}$ in the expression for $P(\alpha, n)$ would yield complicated nonanalytical expressions and $F(\alpha, n)$ would still remain to be computed numerically. When the number of generations gets large, the simple-minded Gaussian model breaks down

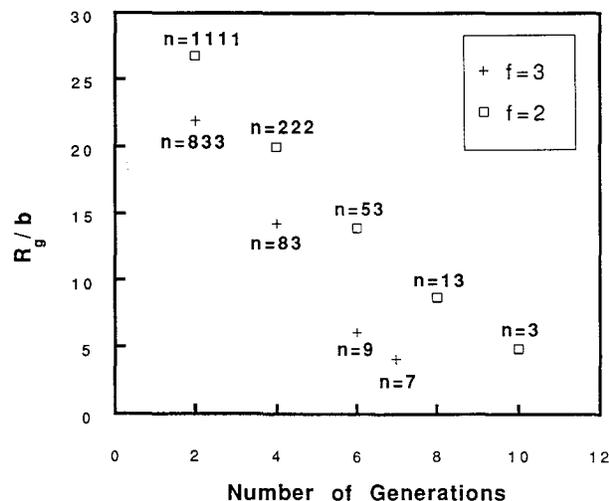


Figure 3. Variation of the relative radius of gyration as extracted from Guinier fits to $S(Q)$ with increasing number of generations. The total number of monomers is kept constant ($N_T = 10,000$) and $N_b = 3$. The two variations correspond to the two cases: $f = 2$ and $f = 3$.

even with the incorporation of excluded volume. Complicated effects as chain stiffness and screening of reacting groups are still not well understood.

Two competing models for the variation of the monomer density inside the dendrimer have been presented.^{4,5} The de Gennes model⁴ predicts an increase of the monomer density which brings about a screening of the reacting groups due to crowding and therefore leads to a termination of the polymerization reactions. This "cauliflower" model assumes that the dendrimer grows outwardly only. On the other hand, computer simulations performed by Lescanec and Muthukumar⁵ report a decrease of the monomer density. They observe a substantial

amount of "turning back" of the growing portions so that after a few generations, the reacting groups could be found not only outside but also inside the dendrimer.

In order to account for intermolecular correlations, "interparticle" interaction models could be used to describe either dendrimer solutions, dendrimer melts or blend mixtures of dendrimers with other polymer components (e.g., linear homopolymer). The mechanics of such models are well known whether these are based on the random phase approximation or on an Ornstein-Zernicke type of approach.

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