# Small-Angle Scattering From Branched Polymers

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The single-polymer form factor is determined for branched polymers using a scaling argument in order to recover the low-Q Porod exponent characteristic of the overall structure. The high-Q Porod exponent characterizes the local branching structure. An alternative approach based on a high-Q expansion contains information about functionality, branch length and branch content. The specific case of a starburst dendrimer for which the form factor is known is discussed. The model predictions are compared to small-angle neutron scattering data from a dilute solution of dendrimer in D_2O.
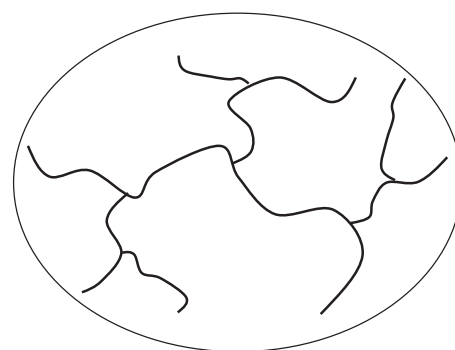
1. Introduction

Modeling branched polymers has been a difficult research undertaking since the advent of polymers. Multifunctional polymerization reactions produce branched structures and chemical cross linking produces networked structures.

The original Stockmayer theory laid out the basic equations describing statistical branching,[1] the Zimm-Stockmayer model for branched polymers derived the mean square radius of gyration for various branched polymers as well as polymer networks containing rings.[2] The modeling of simple (regular) branching has been handled analytically for cases such as star-branched, comb-branched, pom-pom branched, starburst dendrimers, and hyperbranched structures. Approaches have been devised to handle some statistical (random) branching as well using approaches such as the cascade theory.[3,4] More complex branching and polymer networking that contain closed loop structures are harder to model. A generic model of self-assembling chains that includes branching and network formation of arbitrary functionality has been presented using a mean-field approach.[5] A statistical theory of regular (non-random) polycondensation has also been published.[6] Average sizes and conformations can be calculated. Computer simulations have been useful at generating branched polymer architectures with arbitrary multifunctionality, branching schemes and even chain stiffness.[7,8]

Focus of this paper is on modeling of the form factor $P(Q)$ needed for small-angle scattering from branched polymers. Two approaches are used: one based on a simple scaling argument and the other one based on a high-Q expansion (Q being the scattering variable).

2. Model Development

2.1. Fractal Model for Linear Polymers

The fractal model for linear polymers (needed for our modeling approach) is introduced first. Consider a linear polymer chain comprising n monomers and assume excluded volume interactions. The inter-monomer conformational distribution is given by

$$P_L(r_{ij}) = \left(\frac{3}{2\pi \langle r_{ij}^2 \rangle} \right)^{3/2} \exp\left[-\frac{3r_{ij}^2}{2\langle r_{ij}^2 \rangle} \right] \tag{1}$$

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along with

$$\langle r_{ij}^2 \rangle = a^2 |i-j|^{2\nu} \tag{2}$$

where r_{ij} is the inter-monomer distance. Here ν is defined as the excluded-volume parameter and a is the statistical segment length. The single-chain form factor can be calculated as follows[9–11]:

$$
\begin{aligned}
P_L(Q) &= \frac{1}{n^2} \sum_{i,j}^{n} \langle \exp[-i\vec{Q}\cdot\vec{r}_{ij}] \rangle \\
&= \frac{1}{n^2} \sum_{i,j}^{n} \int d\vec{r}_{ij} P(r_{ij}) \exp\left[-i\vec{Q}\cdot\vec{r}_{ij}\right] \\
&= \frac{1}{n^2} \sum_{i,j}^{n} \exp\left[-\frac{Q^2 a^2}{6}|i-j|^{2\nu}\right]
\end{aligned}
\tag{3}
$$

Q is the scattering variable. The following useful identity is used:

$$\sum_{i,j=1}^{n} F(|i-j|) = n + 2\sum_{k=1}^{n}(n-k)F(k) \tag{4}$$

to obtain:

$$P_L(Q) = \frac{1}{n} + \frac{2}{n^2}\sum_{k=1}^{n}(n-k)\exp\left[-\frac{Q^2 a^2}{6}k^{2\nu}\right] \tag{5}$$

For long polymer chains, one can go to the continuous limit (i.e., assume that $n \gg 1$):

$$P_L(Q) = 2\int_0^1 dx(1-x)\exp\left[-U_L x^{2\nu}\right] \tag{6}$$

The following "scattering" variable has been used:

$$U_L = \frac{Q^2 a^2 n^{2\nu}}{6} = \alpha n^{2\nu} \tag{7}$$

where $\alpha = Q^2 a^2/6$ has been introduced. This integral can be performed after defining the incomplete gamma function as:

$$\gamma(d, U_L) = \int_0^{U_L} dt \exp(-t)t^{d-1} \tag{8}$$

The form factor for a linear polymer chain with excluded volume (i.e., following self-avoiding walk statistics) is

therefore:

$$P_L(Q) = \frac{1}{\nu U_L^{1/2\nu}}\gamma(1/2\nu, U_L) - \frac{1}{\nu U_L^{1/\nu}}\gamma(1/\nu, U_L) \tag{9}$$

The high-Q limit of the form factor is given by the asymptotic limit:

$$P_L(Q \to \infty) = \frac{1}{\nu U_L^{1/2\nu}}\Gamma(1/2\nu) - \frac{1}{\nu U_L^{1/\nu}}\Gamma(1/\nu) \tag{10}$$

The gamma function $\Gamma(x) = \gamma(x,\infty)$ has been used. This approach is approximate but yields tractable analytical results.

2.2. Scaling Approach for Branched Polymers

Now, consider a branched polymer consisting of n_t total chain segments of statistical length a. The network is swollen with an excluded volume parameter ν_t corresponding to a mass fractal dimension $d_t = 1/\nu_t$. Consider a "minimum path"[12] corresponding to the main chain backbone comprising n_m chain segments and with excluded volume parameter ν_m and minimum fractal dimension $d_m = 1/\nu_m$ (Figure 1).

A simple scaling argument is used to relate the minimum path to the entire branched polymer.[12]

$$n_t = n_m{}^c \tag{11}$$

Here n_t is the total number of statistical segments in the branched polymer, n_m is the number of segments in the minimum path and c is a scaling exponent.

Note that the branched polymer size and the minimum path scale according to the following mass fractal relations:

$$r \sim n_m{}^{\nu_m} \sim n_t{}^{\nu_t} \tag{12}$$

The last two relations yield the following scaling relations:

$$
\begin{aligned}
d_t &= c d_m \\
\nu_m &= c \nu_t
\end{aligned}
\tag{13}
$$

2.3. Fractal Model for Branched Polymers

Using the fractal model for the minimum path and the scaling relation introduced in the previous section, the single-polymer form factor for the branched polymer becomes:

$$P_B(Q) = \frac{1}{\text{Norm}} 2\int_0^1 dx(1-x)x^{c-1}\exp\left[-U_B x^{2\nu}\right] \tag{14}$$

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Note the introduction of the multiplicative term x^{c-1} which is the ratio n_t/n_m of the total number of segments to the number of segments in the minimum path.

Here the scattering variable depends on the minimum path "length" n_m instead.

$$U_B = \frac{Q^2 a^2 n_m^{2\nu_m}}{6} \tag{15}$$

In order to perform the integral, a change of variable is made:

$$t = U_B x^{2\nu_m}$$
$$dt = 2\nu_m U_B x^{2\nu_m - 1}\, dx \tag{16}$$

After straightforward manipulations, one obtains:

$$P_B(Q) = \frac{1}{\text{Norm}} \left[\frac{1}{\nu_m U_B^{c/2\nu_m}} \gamma(c/2\nu_m, U_B) - \frac{1}{\nu_m U_B^{(c+1)/2\nu_m}} \gamma\big((c+1)/2\nu_m, U_B\big) \right] \tag{17}$$

The high-Q limit is given by:

$$P_B(Q \to \infty) = \frac{1}{\text{Norm}} \left[\frac{1}{\nu_m U_B^{c/2\nu_m}} \Gamma(c/2\nu_m) - \frac{1}{\nu_m U_B^{(c+1)/2\nu_m}} \Gamma\big((c+1)/2\nu_m\big) \right] \tag{18}$$

The normalization factor (Norm) is chosen so that $P_B(Q \to 0) = 1$.

$$\text{Norm} = 2 \int_0^1 dx (1-x) x^{c-1} = \frac{2}{c(c+1)} \tag{19}$$

Recall that the total number of segments in the branched polymer is equal to $n_t = n_m^c$ so that the "branching ratio" is given by $n_t/n_m = n_m^{c-1}$. Note that setting $c = 1$ (i.e., $\nu_t = \nu_m$ or $d_t = d_m$) yields the result for the linear chain case as it should.

2.4. Radii of Gyration and Scattering Variables

The radius of gyration for a linear (not branched) polymer is given by:

$$R_{gL}^2 = \frac{1}{2n^2} \sum_{i,j}^n \langle r_{ij}^2 \rangle = \frac{a^2}{2n^2} \sum_{i,j}^n |i-j|^{2\nu} \tag{20}$$

As before:

$$\langle r_{ij}^2 \rangle = a^2 |i-j|^{2\nu} \tag{21}$$

The same procedure is used for the summation and integration (in the large degree of polymerization limit) to yield:

$$R_{gL}^2 = \frac{a^2}{n} \sum_k^n \left(1 - \frac{k}{n}\right) k^{2\nu} = a^2 n^{2\nu} \int_0^1 dx (1-x) x^{2\nu}$$
$$R_{gL}^2 = \frac{a^2}{(2\nu+1)(2\nu+2)} n^{2\nu} \tag{22}$$

The radius of gyration for a branched polymer is calculated using the same scaling argument as follows:

$$R_{gB}^2 = a^2 n_m^{2\nu_m} \int_0^1 dx (1-x) x^{c-1} x^{2\nu_m}$$
$$R_{gB}^2 = \frac{a^2}{(2\nu_m + c)(2\nu_m + c + 1)} n_m^{2\nu_m} \tag{23}$$

c is the scaling parameter and n_m is the number of segments in the minimum path defined before.

Given the above definitions, the scattering variables are expressed in terms of the radii of gyration as follows:

$$U_L = \frac{Q^2 a^2 n^{2\nu}}{6} = Q^2 R_{gL}^2 \frac{(2\nu+1)(2\nu+2)}{6}$$
$$R_{gL}^2 = \frac{a^2 n^{2\nu}}{(2\nu+1)(2\nu+2)}$$
$$U_B = \frac{Q^2 a^2 n_m^{2\nu_m}}{6} = Q^2 R_{gB}^2 \frac{(2\nu_m + c)(2\nu_m + c + 1)}{6}$$
$$R_{gB}^2 = \frac{a^2 n_m^{2\nu_m}}{(2\nu_m + c)(2\nu_m + c + 1)} \tag{24}$$

Either form (with or without using the radii of gyration) can be used in this model for the scattering from branched polymers.

2.5. The Blob Model

Some polymer systems are characterized by different excluded volume parameters for different length scales. The blob model has been used to model this condition. It has been used, for instance, to model excluded volume effects in semidilute polymer solutions through the concentration blob model[10] whereby chains are swollen between entanglement points and follow ideal chain statistics for length scales larger than the entanglement distance. The blob model is reviewed here in its generality.

Consider a polymer chain comprised of n_2 monomers of segment length a. Blobs containing n_1 monomers each are defined. Two excluded volume parameters are defined: one inside the blobs denoted ν_1 and one outside the blobs

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denoted v_2. The form factor is expressed as before:

$$P(Q) = \frac{1}{n_2{}^2} \sum_{i,j=1}^{n_2} \exp\left[-\frac{Q^2 \langle r_{ij}{}^2 \rangle}{6}\right] \tag{25}$$

The intermonomer distance (squared) is now split into two contributions:

$$\langle r_{ij}{}^2 \rangle = a^2 |i-j|^{2v_1} \text{ for } |i-j| \leq n_1 \text{ (inside each blob)}$$
$$\langle r_{ij}{}^2 \rangle = \xi_1{}^2 \left(\frac{|i-j|}{n_1}\right)^{2v_2} \text{ for } n_1 \leq |i-j| \leq n_2 \text{ (outside the blobs)} \tag{26}$$

Note that the blob size (squared) has been defined as $\xi_1{}^2 = a^2 n_1{}^{2v_1}$. Therefore:

$$P(Q) = \frac{1}{n_2{}^2}\left\{ \sum_{\substack{i,j \\ \text{inside blob}}} \exp\left[-\frac{Q^2 a^2}{6}|i-j|^{2v_1}\right] \right.$$
$$\left. + \sum_{\substack{i,j \\ \text{outside blob}}} \exp\left[-\frac{Q^2 \xi_1{}^2}{6}\left(\frac{|i-j|}{n_1}\right)^{2v_2}\right] \right\} \tag{27}$$

Using the identity introduced before, $P(Q)$ becomes:

$$P(Q) = \frac{1}{n_2{}^2}\left\{ n_2 + 2\sum_{k=1}^{n_1}(n_2 - k)\exp\left[-\frac{Q^2 a^2}{6}|i-j|^{2v_1}\right] \right.$$
$$\left. + 2\sum_{k=n_1+1}^{n_2}(n_2 - k)\exp\left[-\frac{Q^2 \xi_1{}^2}{6}\left(\frac{|i-j|}{n_1}\right)^{2v_2}\right] \right\} \tag{28}$$

Defining the scattering variables (squared) here also as:

$$U_1 = \frac{Q^2 a^2 n_1{}^{2v_1}}{6} \text{ and } U_2 = \frac{Q^2 \xi_1{}^2}{6}\left(\frac{n_2}{n_1}\right)^{2v_2} \tag{29}$$

Approximating the summations by integrations (but keeping n_1 and n_2 finite), one obtains:

$$P(Q) = \frac{1}{n_2{}^2}\left\{ n_2 + 2n_1{}^2 \int_{\frac{1}{n_1}}^{1} dx \left(\frac{n_2}{n_1} - x\right)\exp\left[-U_1 x^{2v_1}\right] \right.$$
$$\left. + 2n_2{}^2 \int_{\frac{n_1+1}{n_2}}^{1} dx'(1 - x')\exp\left[-U_2 x'^{2v_2}\right] \right\} \tag{30}$$

The variable changes $x = k/n_1$ and $x' = k/n_2$ have been performed. The integration variables are modified as

follows:

$$t = U_1 x^{2v_1} \text{ and } t' = U_2 x'^{2v_2} \tag{31}$$

After a couple of manipulations, the following result is reached:

$$P(Q) = \frac{1}{n_2{}^2}\left[n_2 + n_1{}^2\left\{ \frac{1}{v_1 U_1{}^{1/2v_1}}\frac{n_2}{n_1}F_1\left(\frac{1}{2v_1}, U_1\right) \right.\right.$$
$$\left. - \frac{1}{v_1 U_1{}^{1/v_1}}F_2\left(\frac{1}{v_1}, U_1\right) \right\}$$
$$+ n_2{}^2\left\{ \frac{1}{v_2 U_2{}^{1/2v_2}}F_3\left(\frac{1}{2v_2}, U_2\right) \right.$$
$$\left.\left. - \frac{1}{v_2 U_2{}^{1/v_2}}F_4\left(\frac{1}{v_2}, U_2\right) \right\}\right] \tag{32}$$

The following functions have been defined:

$$F_1\left(\frac{1}{2v_1}, U_1\right) = \int_{\frac{U_1}{n_1{}^{2v_1}}}^{U_1} dt\, t^{\frac{1}{2v_1}-1}\exp(-t) = \gamma\left(\frac{1}{2v_1}, U_1\right)$$
$$- \gamma\left(\frac{1}{2v_1}, U_1\left(\frac{1}{n_1}\right)^{2v_1}\right)$$

$$F_2\left(\frac{1}{v_1}, U_1\right) = \int_{\frac{U_1}{n_1{}^{2v_1}}}^{U_1} dt\, t^{\frac{1}{v_1}-1}\exp(-t) = \gamma\left(\frac{1}{v_1}, U_1\right)$$
$$- \gamma\left(\frac{1}{v_1}, U_1\left(\frac{1}{n_1}\right)^{2v_1}\right)$$

$$F_3\left(\frac{1}{2v_2}, U_2\right) = \int_{U_2\left(\frac{n_1+1}{n_2}\right)^{2v_2}}^{U_2} dt'\, t'^{\frac{1}{2v_2}-1}\exp(-t') = \gamma\left(\frac{1}{2v_2}, U_2\right)$$
$$- \gamma\left(\frac{1}{2v_2}, U_2\left(\frac{n_1+1}{n_2}\right)^{2v_2}\right)$$

$$F_4\left(\frac{1}{v_2}, U_2\right) = \int_{U_2\left(\frac{n_1+1}{n_2}\right)^{2v_2}}^{U_2} dt'\, t'^{\frac{1}{v_2}-1}\exp(-t') = \gamma\left(\frac{1}{v_2}, U_2\right)$$
$$- \gamma\left(\frac{1}{v_2}, U_2\left(\frac{n_1+1}{n_2}\right)^{2v_2}\right) \tag{33}$$

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These functions have been expressed in terms of the incomplete gamma function $\gamma(d, U)$ defined before. Note that this function simplifies for integer fractal dimensions:

$$
\begin{aligned}
\gamma(1, U) &= 1 - \exp(-U) \\
\gamma(2, U) &= -U\exp(-U) - \exp(-U) + 1 \\
\gamma(3, U) &= -U^2\exp(-U) + 2[-U\exp(-U) - \exp(-U) + 1]
\end{aligned}
\tag{34}
$$

2.6. Blob Model for Branched Polymers

In order to capture the two-length scale feature, the blob model is used to describe branched polymers. A blob is defined between two adjacent branch points. This model captures the two-length-scale feature whereby the local length scale (index 1) could have a different fractal dimension and the branched polymers feature described by the second length scale (index 2) is based on the scaling argument described above.

$$
\begin{aligned}
P(Q) = \frac{1}{\text{Norm}} \frac{1}{n_2{}^2} \Bigg[n_2 + n_1{}^2 \Bigg\{ & \frac{1}{\nu_1 U_1{}^{1/2\nu_1}} \frac{n_2}{n_1} F_1\left(\frac{1}{2\nu_1}, U_1\right) \\
& - \frac{1}{\nu_1 U_1{}^{1/\nu_1}} F_2\left(\frac{1}{\nu_1}, U_1\right) \Bigg\} \\
+ n_2^2 \Bigg\{ & \frac{1}{\nu_2 U_2{}^{c/2\nu_2}} F_3\left(\frac{c}{2\nu_2}, U_2\right) \\
& - \frac{1}{\nu_2 U_2{}^{(c+1)/\nu_2}} F_4\left(\frac{c+1}{\nu_2}, U_2\right) \Bigg\} \Bigg]
\end{aligned}
\tag{35}
$$

This is a general result describing the form factor for branched polymers.

For large degrees of polymerization ($n_2 > n_1 \gg 1$), this result simplifies to:

$$
\begin{aligned}
P(Q) = \frac{1}{\text{Norm}} \Bigg[& \frac{n_1}{n_2} \frac{1}{\nu_1 U_1{}^{1/2\nu_1}} F_1\left(\frac{1}{2\nu_1}, U_1\right) \\
& - \frac{n_1{}^2}{n_2{}^2} \frac{1}{\nu_1 U_1{}^{1/\nu_1}} F_2\left(\frac{1}{\nu_1}, U_1\right) \\
& + \frac{1}{\nu_2 U_2{}^{c/2\nu_2}} F_3\left(\frac{c}{2\nu_2}, U_2\right) \\
& - \frac{1}{\nu_2 U_2{}^{(c+1)/\nu_2}} F_4\left(\frac{c+1}{\nu_2}, U_2\right) \Bigg]
\end{aligned}
\tag{36}
$$

This result applies to long-branch polymers with a large number of branches. The F functions also simplify in the large-n limit ($n_2 > n_1 \gg 1$) to:

$$
\begin{aligned}
F_1\left(\frac{1}{2\nu_1}, U_1\right) &= \gamma\left(\frac{1}{2\nu_1}, U_1\right) \\
F_2\left(\frac{1}{\nu_1}, U_1\right) &= \gamma\left(\frac{1}{\nu_1}, U_1\right) \\
F_3\left(\frac{c}{2\nu_2}, U_2\right) &= \gamma\left(\frac{c}{2\nu_2}, U_2\right) - \gamma\left(\frac{c}{2\nu_2}, U_2\left(\frac{n_1}{n_2}\right)^{2\nu_2}\right) \\
F_4\left(\frac{c+1}{2\nu_2}, U_2\right) &= \gamma\left(\frac{c+1}{2\nu_2}, U_2\right) - \gamma\left(\frac{c}{2\nu_2}, U_2\left(\frac{n_1}{n_2}\right)^{2\nu_2}\right)
\end{aligned}
\tag{37}
$$

Here also the normalization factor (Norm) is chosen so that $P(Q \to 0) = 1$.

$$
\begin{aligned}
\text{Norm} = \frac{1}{n_2^2} \Bigg\{ & n_2 + 2n_1^2 \int_{\frac{1}{n_1}}^{1} dx \left(\frac{n_2}{n_1} - x\right) \\
& + 2n_2{}^2 \int_{\frac{n_1+1}{n_2}}^{1} dx'(1-x')x'^{(c-1)} \Bigg\}
\end{aligned}
\tag{38}
$$

Figure 2 contains plots of the normalized form factor when the branching scaling exponent is varied. The excluded volume parameters are taken to be $\nu_1 = \nu_2 = 0.6$ which corresponds to a high-Q Porod exponent $d_1 = 1/\nu_1 = 5/3$ (fully swollen chain portions). The low-Q Porod exponent is given by cd_1 in each case (mass fractal branched polymer). When used on high quality data that contain both the low-Q and high-Q features, one could back out the branch length n_1, the scaling exponent c (ratio of the low-Q to the high-Q Porod exponents) and the branch content given by n_2^c.

This scaling approach reproduces the two Porod exponents; one for correlations inside the blobs (at high-Q) and one for the entire branched polymer (at low-Q). It, however, cannot yield information about the functionality of the branched polymer. Another approach is presented next.
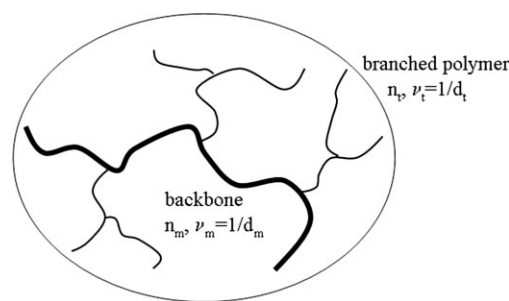

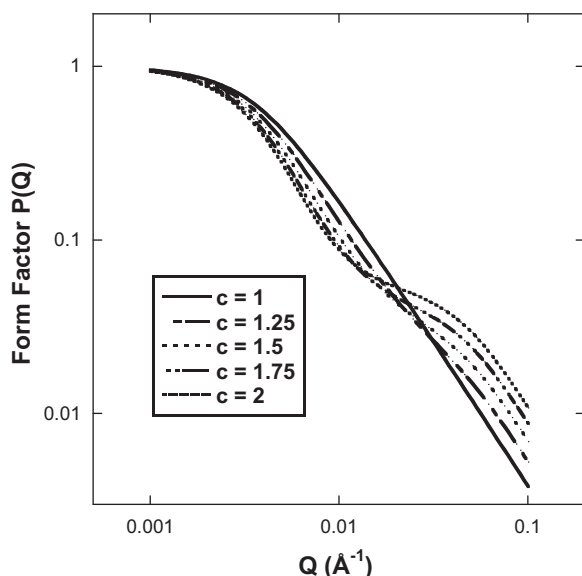**Figure 1.** Schematics of the branched polymer showing the minimum path (backbone) in dark.

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Macromol. Theory Simul. **2012**, DOI: 10.1002/mats.201100111
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Figure 2. Form factor for branched polymer with $v_1 = v_2 = 0.6$, $n_1 = 100$, $n_2 = 10\,000$, and $a = 4$ Å. The scaling exponent c is varied from $c = 1$ (for linear polymers with no branching) to $c = 2$ (for highly branched polymer).

2.7. An Alternative Approach to Describe Branched Polymers

Another approach[13] is followed here to describe the form factor for a regularly branched polymer (with no loops). This approach focuses on the high-Q expansion.

The high-Q expansion for the form factor for a simple linear Gaussian chain (for which $v = 1/2$) is given by:

$$P_L(Q \to \infty) = -\frac{2}{(\alpha n)^2} + \frac{2}{(\alpha n)} \tag{39}$$

$$\alpha = \frac{Q^2 a^2}{6}$$

This high-Q asymptotic limit is obtained by removing the exponential term from the so-called Debye function and keeping only the $1/Q^2$ and the $1/Q^4$ terms.

Consider a regularly branched polymer with n segments per branch (each segment of size a), and functionality f (i.e., there are f branches connected to each branch point). There are summations over monomers within each branch and summations over monomers in different branches. If there are s total branches containing n monomers each, the (non-normalized) scattering function contains two main terms:

$$\Im(Q) = \frac{1}{sn}\left[\sum_{\beta=\gamma}^{s}\sum_{i,j}^{n}\ldots + \sum_{\beta\neq\gamma}^{s}\sum_{i,j}^{n}\ldots\right] \tag{40}$$

The summation over Greek letters is over branches while the summation over Roman letters is over monomers in each branch. The first term involves the Debye function and its high-Q expansion. The second term involves the product $F(Q)E(Q)F(Q)$ where the following form factor amplitude $F(Q)$ and propagator $E(Q)$ have been defined:

$$F(Q) = \frac{1 - \exp(-\alpha n)}{(\alpha n)}$$
$$E(Q) = \exp(-\alpha n) \tag{41}$$

$F(\alpha)$ involves one monomer summation over a branch while $E(\alpha)$ represents the propagation over the intermediate branches (without any monomer summation) as shown in Figure 3.

The high-Q expansion is obtained by setting the exponential factors equal to zero. The entire product $F(Q)E(Q)F(Q)$ becomes equal to zero except for the case of adjacent branches for which $E(Q) = 1$. The total number of adjacent branch pairs in the polymer is equal to $bf(f-1)$ where b is the total number of branch points. Adding the two contributions (summations over the same branch and over different branches) yields the following high-Q expansion:[13]

$$\Im(Q \to \infty) = \frac{1}{sn}\left[sn^2\left(\frac{-2}{(\alpha n)^2} + \frac{2}{(\alpha n)}\right) + n^2\frac{bf(f-1)}{(\alpha n)^2}\right]$$
$$= \left(\frac{-2}{n\alpha^2} + \frac{2}{\alpha}\right) + \frac{bf(f-1)}{sn\alpha^2} \tag{42}$$

The parameters s (total number of branches), b (total number of branch points) and f (functionality) can be related as follows. There are f branches connected to the first branch point (chosen randomly) but there are $(f-1)$ branches connected to the remaining $(b-1)$ branch points. The total number of branches s is therefore the sum
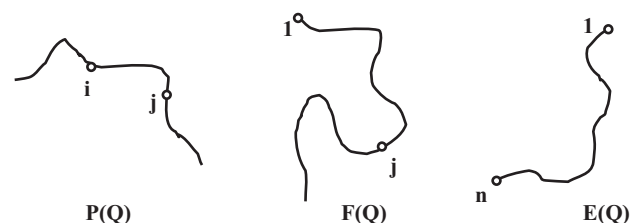

Figure 3. Schematic representation of the summations over monomers for the various scattering factors for Gaussian polymer chains.

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$s = f + (b-1)(f-1)$ or simply $s = 1 + b(f-1)$. Therefore,

$$\Im(Q \to \infty) = \left(\frac{-2}{n\alpha^2} + \frac{2}{\alpha}\right) + \frac{(s-1)f}{sn\alpha^2}$$
$$= \frac{2}{\alpha} + \frac{1}{n\alpha^2}\left[f - 2 - \frac{f}{s}\right] \tag{43}$$

The $1/\alpha^2$ term contains valuable information. For example, the Zimm plot consists in plotting $1/\Im(Q)$ versus $\alpha/2$ which in the high-Q limit gives:

$$\frac{1}{\Im(Q \to \infty)} = \frac{\alpha}{2} - \frac{1}{4n}\left[-2 + f - \frac{f}{s}\right] \tag{44}$$

The intercept of the Zimm plot $-(1/4n)[-2 + f - f/s]$ contains information about branching. For large branched macromolecules, $f/s << 1$, and the intercept reduces to $-(1/4n)[-2 + f]$. If the number of segment lengths per branch n is known, one can obtain the functionality f and vice versa.

2.8. Including Polydispersity

Polydispersity can affect all parameters n, f, b (or s). Since it is hard to include all these effects, focus here will be on polydispersity in n and f. Since polydispersity in the length of each branch n and polydispersity in the functionality f are independent of the polymer architecture, these could be averaged separately.[13] The branch length polydispersity is represented by the number-average $\bar{n} = \sum_i n_i w_i / \sum_i w_i$. If one assumes linear deviation from average functionality $f = \bar{f} + \Delta f$, accounting for polydispersity in f involves the product: $\overline{f(f-1)} = \bar{f}(\bar{f}-1) + \overline{\Delta f^2}$ where $\overline{\Delta f} = 0$ has been eliminated (by definition) and $\overline{\Delta f^2}$ represents the variance of the functionality distribution. The result with polydispersity included follows:

$$\Im(Q \to \infty) = \frac{2}{\alpha} + \frac{1}{\bar{n}\alpha^2}\left[\bar{f} - 2 + \frac{\overline{\Delta f^2}}{\bar{f}-1} - \frac{1}{s}\left(\bar{f} + \frac{\overline{\Delta f^2}}{\bar{f}-1}\right)\right] \tag{45}$$

2.9. Reintroducing Excluded-Volume Effects

Based on the previous discussions, one can introduce the excluded volume effect into the high-Q approach. In the simple case of linear chains, recognizing that $\Im(Q) = nP_L(Q)$, one obtains the following high-Q expansion:

$$\Im(Q \to \infty) = \frac{1}{\nu\alpha^{1/2\nu}}\Gamma(1/2\nu) - \frac{1}{\nu\alpha^{1/\nu}}\Gamma(1/\nu) \tag{46}$$

In the case of a regularly branched polymer for which $\Im(Q) = snP(Q)$, the ad-hoc result is:

$$\Im(Q \to \infty)$$
$$= \frac{1}{\nu\alpha^{1/2\nu}}\Gamma(1/2\nu) - \frac{1}{n\alpha^{1/\nu}}\left[f - \frac{1}{\nu}\Gamma(1/\nu) - \frac{f}{s}\right] \tag{47}$$

Note that when excluded volume is included (i.e., for good-solvent conditions), the simple factorization $F(Q)E(Q)F(Q)$ used for Gaussian chains is only approximate.

2.10. Starburst Dendrimers

The case of starburst dendrimers is a typical case of regularly branched polymers. It is used here to get some insight into the methods discussed above. The form factor has been calculated.[14] Consider a dendrimer with N_b major branches that start the dendrimer growth (for example $N_b = 3$). Each major branch contains N_g generations (the case $N_g = 5$ will be considered). Correlations within a single local branch (block) are called S_{sb}^s, those within the same major branch going forward are called S_{sb}^f, those within the same major branch going across are called S_{ab}^a, and interbranch correlation are called S_{ib} (Figure 4).

The single block form factor is given by:

$$P(\alpha n) = 2\frac{[\exp(-\alpha n) - 1 + \alpha n]}{(\alpha n)^2}$$
$$S_{sb}^s(Q) = \frac{(f-1)^{N_g} - 1}{f-2}n^2 P(\alpha n) \tag{48}$$

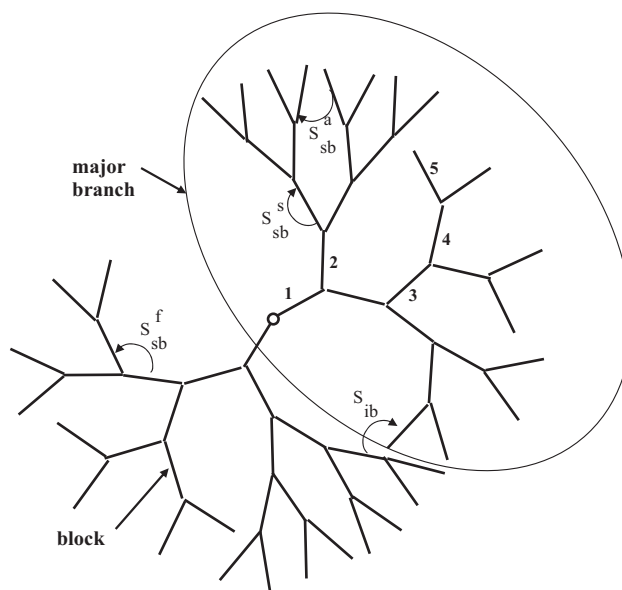*Figure 4.* Schematic representation of a starburst dendrimer showing two major branches.

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Macromol. Theory Simul. **2012**, DOI: 10.1002/mats.201100111
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Here $(f-1)^{N_g} - 1 \big/ (f-2)$ is the total number of blocks per branch. The form factor amplitude for a single block is given by:

$$F(\alpha n) = \frac{1 - \exp(\alpha n)}{(\alpha n)} \tag{49}$$

The various contributions involve the following summations:[14]

$$S_{sb}^{f}(Q) = 2|nF(\alpha n)|^2 \sum_{k=1}^{N_g} (f-1)^{k-1} \sum_{l=k+1}^{N_g} (f-1)^{l-k} \exp[-\alpha n(l-k-1)]$$

$$S_{sb}^{a}(Q) = 2|nF(\alpha n)|^2 \sum_{k=2}^{N_g} (f-1)^{k-1} \sum_{m=1,3}^{2k-3} (f-2)(f-1)^{(m-1)/2} \exp[-\alpha n(m-1)] * \left\{ 1 + 2 \sum_{i=k+1}^{N_g} (f-1)^{l-k} \exp[-\alpha n(l-k)] \right\}$$

$$S_{ib}(Q) = |nF(\alpha n)|^2 \sum_{k=1}^{N_g} (f-1)^{k-1} \sum_{l=1}^{N_g} (f-1)^{l-1} \exp[-\alpha n(l+k-2)]$$

$$\tag{50}$$

The dendrimer form factor is obtained by gathering all contributions:

$$P(Q) = \frac{N_b \left[S_{sb}^{s}(Q) + S_{sb}^{f}(Q) + S_{sb}^{a}(Q) \right] + N_b(N_b - 1)S_{ib}(Q)}{\dfrac{1}{f-2} nN_b \left[(f-1)^{N_g} - 1 \right]} \tag{51}$$

Note that $s = nN_b[(f-1)^{N_g} - 1] \big/ (f-2)$ is the total number of blocks in the dendrimer. The various summations are performed using the Mathematica software. In order to check that all needed term have been included, the limit $\alpha = 0$ is taken. For the following parameters: $n = 1$, $f = 3$, $N_b = 3$, $N_g = 5$, one obtains the following block pairs: $S_{sb}^{f} = 196$, $S_{sb}^{a} = 1468$, $S_{ib} = 961$. The number of blocks per branch is: $S_{sb}^{s} = 31$. The total number of blocks is $s = 93$ and the total number of branch points (where two blocks come together) is $b = 46$ ($= 3 \times 15 + 1$). This analysis results in a Porod plot, a Zimm plot and a modified Kratky plot (Figure 5–7).

For the case with functionality $f = 2$ (no branching), one recovers the result for linear polymer for which the high-Q limit has a Porod exponent of -2. The high-Q expansion yields an extrapolated intercept in the Zimm plot which is positive. When the functionality increases to $f = 3$ (doubling the number of blocks at each dendrimer generation), the high-Q Porod exponent is around -3. This gives an estimate of the scaling exponent $c \approx 3/2 = 1.5$. The $P(Q) \sim 1/Q^3$ region, however, is rather narrow, squeezed between the $1/Q^4$ and the $1/Q^2$ regions. Note that Porod exponents between 3 and 4 are conventionally associated with "surface fractals" whereas this (dendrimer) case involves no surface at all. This shows that mass fractal Porod exponents can be higher than 3 for branched polymers.

In order to compare this model with experimental data, small-angle neutron scattering (SANS) data from a fifth-generation poly(amidoamine) (PAMAM) dendrimer in D_2O solution are used. SANS data were taken for four dendrimer volume fractions in the dilute regime then extrapolated to the infinite dilution limit (i.e., to zero volume fraction) in order to isolate the single dendrimer form factor $P(Q)$. A Zimm plot of the inverse form factor $1/P(Q)$ versus Q^2 in a high-Q region ($Q > 0.076$ Å^{-1}) window yields an extrapolated measured intercept around -22.2 as shown in Figure 8. This intercept is in agreement with the calculated value of -22.5 reported in Table 1. Alternatively,
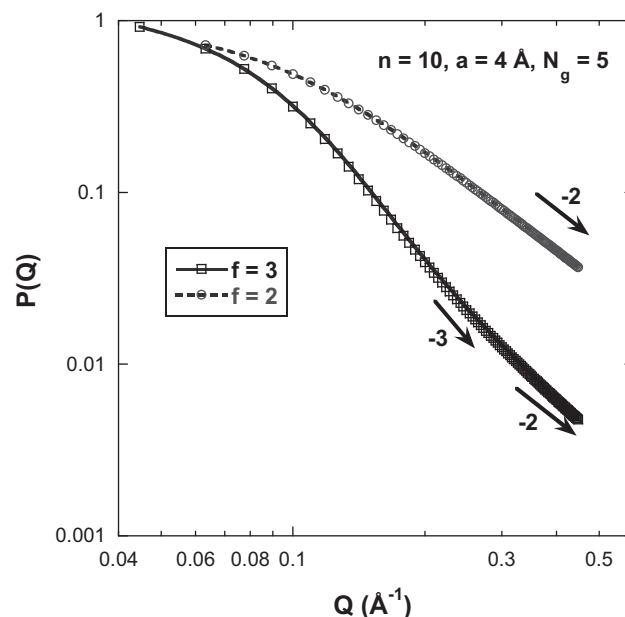

Figure 5. Porod Plot for starburst dendrimer with $n = 10$ (10 monomers per block), $a = 4$ Å (a is the statistical segment length), and $N_g = 5$ (five generations). The top curve corresponds to $f = 2$ (linear chain) and $N_b = 2$ (two major branches). The bottom curve corresponds to $f = 3$ (number of monomers doubles at each generation) and $N_b = 3$ (three major branches start the dendrimer growth).

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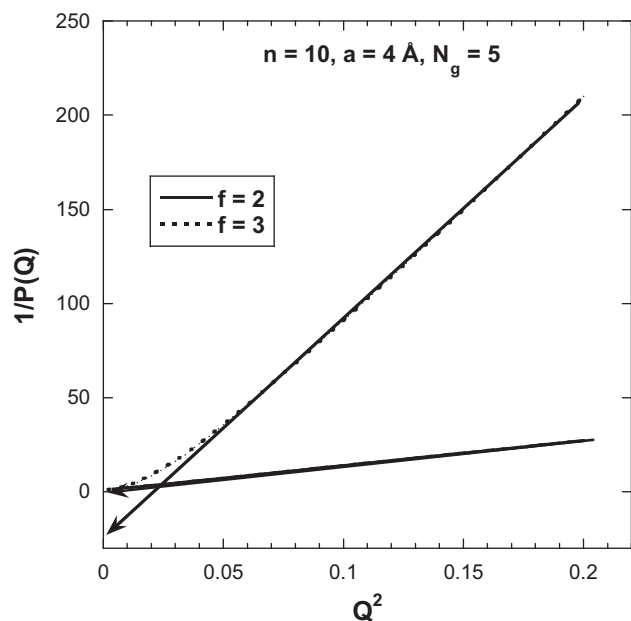
Figure 6. Zimm Plot for starburst dendrimer for the same conditions as in the previous figure. Note that for $f = 2$, the high-Q extrapolation intercept is positive while for $f = 3$, it is negative.

Figure 8. Zimm plot from SANS data for fifth-generation PAMAM dendrimer solution in D_2O extrapolated to the infinite dilution limit (zero concentration). A linear fit of the high-Q data yields an intercept around -22.2. Statistical error bars correspond to one standard deviation.

setting a dendrimer functionality $f = 3$, one obtains from the relationship $s = (f/4 - \mathrm{int}\,ercept)\cdot4/(f - 2)$ the total number of branches $s = 92$ which is close to the calculated value $s = 93$ for the fifth-generation dendrimer.

Figure 7. Modified Kratky plot for starburst dendrimer for the same conditions as in the previous figure. The $P(Q) \sim 1/Q^3$ region is clearly observed. The regions right before and right after this region correspond to the scaling $P(Q) \sim 1/Q^d$ with Porod exponents $d > 3$ and $d < 3$, respectively.
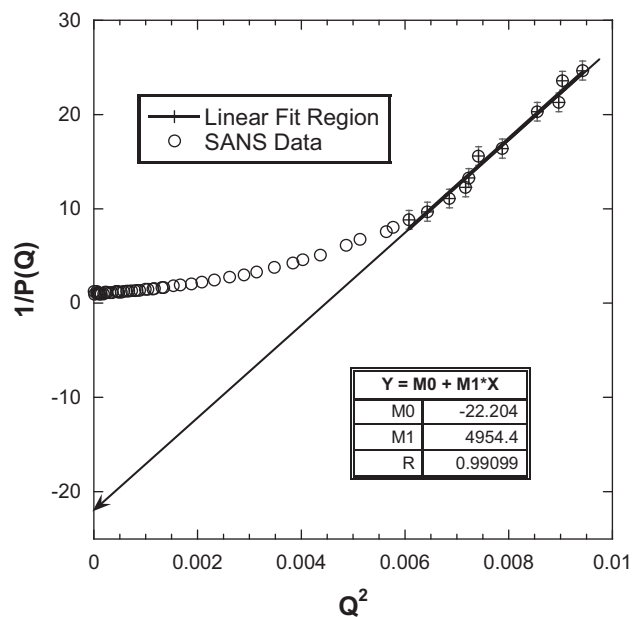
Table 1. Intercept of the Zimm Plot for a dendrimer for $n = 10$, $a = 4$ Å and $N_g = 5$.

Functionality f	Number of branches N_b	Total number of blocks s	Intercept $-\dfrac{s}{4}\left(f - 2 - \dfrac{f}{s}\right)$
2	2	10	0.50
3	3	93	−22.5

3. Discussion

Two approaches have been used to model polymer branching. The first approach uses a simple scaling argument, assumes random branching, and yields no information about the functionality. The second approach uses a high-Q expansion for regularly branched polymers, assumes no closed loops, and contains information about the functionality and branch length as well as branch content. The effect of polydispersity has been included. Each approach has its limitations. The high-Q expansion approach considers the $1/Q^2$ and $1/Q^4$ terms only. These correspond to correlations between neighboring branches. In practice, other correlations would contribute as well. On the other hand, the scaling approach is supposed to implicitly include

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such contributions. It, however, cannot yield information about functionality. Both approaches suffer from shortcomings. It is, for instance, difficult to find pure scaling regions (with linear behavior in a Porod plot) over a wide Q range. Branched polymers are complex systems to model; the tractable approaches described here constitute another contribution.

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