Statistics of Star-Shaped Molecules. I. Stars with Polydisperse Side Chains

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ABSTRACT: The cascade theory has been applied for the calculation of averages of star-shaped molecules, which can be measured by light scattering, *i.e.*, the weight-average molecular weight M_w, and the z averages of the mean-square radius of gyration $\langle S^2\rangle_z$ and of the particle scattering factor $P_z(\Theta)$. The study considers stars with large spherical centers (microgel) whose chemical composition differs from that of the side chains. The centers are homodisperse in size while the linear side chains exhibit a Schulz–Flory distribution. Chain stiffness is taken into account but is restricted to stiff side chains which are linked to the center by free joints. In all cases analytic expressions are derived for the true and apparent molecular and conformational averages.

In the last decade the investigation of star molecules has been the subject of repeated interest. The preparation of these simplest branched structures appeared attractive especially to chemists because homodisperse molecules with a definite number of side chains should be accessible to synthesis by the technique of anionic polymerization[1-20] and these well-defined polymers would be ideal for extensive tests of existing theories.[21-29] Experience has shown, however, that well-defined samples cannot be prepared as easily as was at first thought. Frequently the number of side chains is not identical for all molecules and consequently a certain polydispersity is obtained.

It appeared desirable, therefore, to extend the existing theories of Benoit,[22] Berry and Orofino,[26] and Casassa and Berry[28] to more general cases in which various kinds of polydispersity, a certain chain stiffness, and various types of molecules are included, and in which the star center is relatively large and different in chemical composition from the grafted side chains (copolymers).

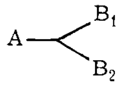
For the solution of this problem the cascade theory of Good[30,31] and of Gordon[32-34] seems to be most appropriate for two main reasons. First, in this theory the molecular weight, the mean-square radius of gyration, and the particle scattering factor are only special cases of a general function. Second, it yields averages which are directly measurable by common techniques, *e.g.*, the weight average of the molecular weight, and the z averages of the mean-square radius of gyration and the particle scattering factor. Furthermore, this theory results in analytic expressions which are often simple and are not restricted to either large degrees of polymerization or to Gaussian behavior, as was the case in earlier theories.[21-29]

In the following, explicit calculations are performed for stars with polydisperse linear side chains exhibiting a most probable distribution for the chain length. From the theoretical standpoint this case is easier to handle than the corresponding homodisperse stars. It is also of experimental interest, because such polydisperse side chains are grafted during free radical polymerization in the presence of a polyfunctional chain transfer agent. The more complicated case of stars with homodisperse side chains will be treated in part II.

No attempt is made, however, to take into account excluded volume effects.

Some General Considerations Concerning a Molecular Assembly

The principles for the use of the cascade theory were displayed in papers of Gordon and his coworkers[32-38] and in papers on the calculation of the particle scattering factors for randomly branched polycondensates[34] and for polymers built up of units of type



Following these principles one first has to choose any unit of a branched molecule as the root of a tree. This generates, from the molecular assembly, a statistical forest of trees in which each molecule, of degree of polymerization x, is represented x times rooted once in each of its units. Such a set of x trees is called a *clone.*[40] Let $n(x)$ be the frequency of molecules of degree of polymerization x in the actual chemical system. Then the corresponding clone in the statistical forest represents the weight fraction $w(x) \propto xn(x)$.

The chemical nature of the central unit in star molecules may be different from the units in the side chains. Under these conditions the statistical forest can be partitioned into trees having either units c (center of the star) or s (units of the side chains) as roots. This is schematically demonstrated in Figure 1. The number fractions in the statistical forest of all c-rooted trees, w_c, and of all s-rooted trees, w_s, follow from the identity

$$\frac{\sum xn(x)}{\sum xn(x)} = \frac{\sum\limits_{x_c=1}^{\infty} x_c n(x)}{\sum\limits_{x=1}^{\infty} xn(x)} + \frac{\sum\limits_{x_s=1}^{\infty} x_s n(x)}{\sum\limits_{x=1}^{\infty} xn(x)} = w_c + w_s = 1 \tag{1a}$$

where

$$x_c + x_s = x \tag{2}$$

Thus x_c is the number of c-rooted and x_s the number of s-rooted trees for a molecule of DP = x. The number-fraction distributions can be easily calculated, since it is the convolution of the frequency distribution of the $\bar{f}$, say, side chains with that of the center. Thus, the frequency distribution of the star molecules is

$$n(x) = n(x_c)^* n(x_s)^{\bar{f}*} \tag{3}$$

where the asterisks signify convolution and the exponent $\bar{f}*$ means an f-fold convolution of $n(x_s)$ (see Feller).[43] In terms of generating functions defined as follows

$$H_c(\theta) = \sum n(x_c)\theta^{x_c}$$

$$H_s(\theta) = \sum n(x_s)\theta^{x_s}$$

$$H(\theta) = \sum n(x)\theta^{x}$$

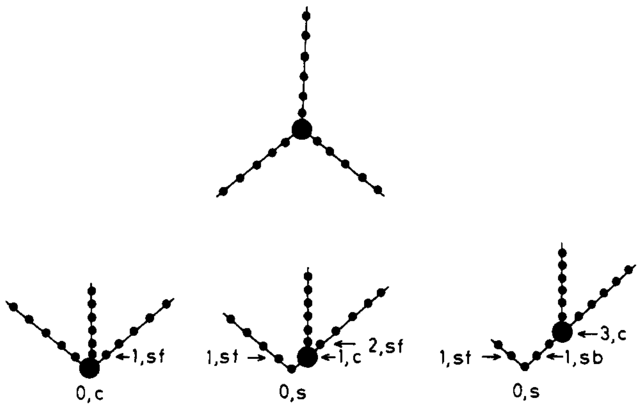


Figure 1. Graph of a three-star molecule (above) and three rooted tree representations (below). The first index indicates the number of the generation to which a repeat unit belongs; s or c designates the type of unit, sb denotes a repeat unit s that belongs to a branch bearing the central unit c at its end, and sf denotes a unit s belonging to a branch with a free end.

eq 3 becomes

$$H(\theta) = H_c(\theta)[H_s(\theta)]^{\bar{f}} \tag{4}$$

Differentiation at $\theta = 1$ yields

$$\sum xn(x) = \sum x_c n(x_c) + \bar{f}\sum x_s n(x_s)$$

$$\mathrm{DP}_n = \mathrm{DP}_{nc} + \bar{f}\mathrm{DP}_{ns} \tag{5}$$

Comparison with eq 1a leads to the relationships

$$w_c = \frac{\mathrm{DP}_{nc}}{\mathrm{DP}_{nc} + \bar{f}\mathrm{DP}_{ns}}\ ;\ w_s = \frac{\bar{f}\mathrm{DP}_{ns}}{\mathrm{DP}_{nc} + \bar{f}\mathrm{DP}_{ns}} \tag{6a}$$

DP_{nc} and DP_{ns} are the number-average degrees of polymerization of the center and of the grafted side chains, and DP_n is the resulting number-average degree of polymerization of the stars.

Equation 1a applies only if each unit of a molecule has the same chance of becoming the root of a tree. In physical experiments this is not always true, but the repeat units are weighted according to their mass. This means a c unit has the relatively higher chance M_c/M_s of becoming a root than an s unit, if the mass M_c is larger than M_s.

The corresponding *mass fractions* follow now from the identity

$$\frac{\sum M_x n(x)}{\sum M_x n(x)} = \frac{M_c \sum_{x_c=1}^{\infty} x_c n(x)}{\sum M_x n(x)} + \frac{M_s \sum_{x_s=1}^{\infty} x_s n(x)}{\sum M_x n(x)} = m_c + m_s \tag{1b}$$

and are

$$m_c = \frac{M_{nc}}{M_{nc} + \bar{f}M_{ns}}\ ;\ m_s = \frac{\bar{f}M_{ns}}{M_{nc} + \bar{f}M_{ns}} \tag{6b}$$

where M_{nc} and M_{ns} are the number-average molecular weights of the star center and the side chains. Evidently, these equations are also valid for comb molecules; in the following, however, the star center is considered as one unit of high molecular weight, in which case $x_c = 1$.

Number fractions and mass fractions are obtained here in an elementary way with reference to a special case. In a recent paper Gordon, *et al.*,[42] derived a basic theorem from which the weight fractions can be calculated quite generally from the link probability generating functions. These functions lead also to the calculation of higher molecular averages and are introduced in the following section.

It will be noticed that the weight-average degree of polymerization could be derived by a two-fold differentiation of eq 4 at $\theta = 1$. For the calculation of conformational averages, which is the purpose of this paper, the more comprehensive cascade theory is required.

The Link Probability Generating Functions

A further stage in the calculation of the mean structure of a tree in Figure 1 is achieved by setting up the probability generating functions for the various generations. The root of a tree may be designated the zeroth generation; repeat units linked to the root are then members of the first generation and the additional units linked to the members of the first generation form the population of the second generation, etc.

Starting with the f-functional star center as root, one has for each functionality the probability α that it has reacted with an s unit and the probability $1 - \alpha$ for no reaction. According to the definition of a generating function the probabilities of a distribution occur as coefficients in the power series expansion in terms of the auxiliary variable θ; therefore θ^0 indicates no reaction, θ^1 reaction with one functionality, θ^2 reaction with two functionalities, etc. Thus, the generating function for a single functionality of a star center is

$$F_a(\theta) = 1 - \alpha + \alpha\theta_{sf} \tag{7}$$

and the link probability generating function for the star center as a whole is the f-fold convolution of F_a and reads

$$F_{0c}(\theta) = (1 - \alpha + \alpha\theta_{sf})^f \tag{8}$$

The index sf of the auxiliary variable indicates that the reaction took place with an s unit from a chain, which has one free end (Figure 1, bottom left).

Concerning trees with s units as roots one realizes from Figure 1 that these trees have two branches which are not alike, because the one branch leads to a free end, while the other branch must eventually lead to the star center. Therefore, the link generating function results from the convolution of the two different branching possibilities and is the product of the free-end generating function

$$F_{sf}(\theta) = 1 - \beta + \beta\theta_{sf}$$

and the bound-end generating function

$$F_{sb}(\theta) = (1 - \beta)\theta_c + \beta\theta_{sb}$$

and reads

$$F_{0s}(\theta) = [1 - \beta + \beta\theta_{sf}][(1 - \beta)\theta_c + \beta\theta_{sb}] \tag{8b}$$

In these equations β is the probability for reaction of an s unit with another s unit, and $1 - \beta$ is the probability for no reaction with an s unit. Thus, $1 - \beta$ signifies the end of a chain reaction *before* deactivation by chain coupling or by another termination reaction. Chain coupling to the star center is indicated by the factor θ_c^1 (bound end), while all other termination reactions are indicated by the factor $\theta_c^0 = 1$ (free end).

To set up the probability generating functions for the number of offspring of individuals on the first generation and of all further generations, one has to take into account that one functionality has already been used to link such a unit to its "parent" in the preceding generation. Thus

$$F_{nc}(\theta) = (1 - \alpha + \alpha\theta_{sf})^{f-1} \tag{9a}$$

$$F_{nsf}(\theta) = 1 - \beta + \beta\theta_{sf} \tag{9b}$$

$$F_{nsb}(\theta) = (1 - \beta)\theta_c + \beta\theta_{sb} \tag{9c}$$

The required mass fractions can be calculated either from eq 6 or from the condition (basic theorem of Gordon[40,43])

$$w_c \frac{\partial F_{0c}}{\partial \theta_s}\bigg|_{\theta_c=\theta_s=1} = w_s \frac{\partial F_{0s}}{\partial \theta_c}\bigg|_{\theta_c=\theta_s=1} \tag{10}$$

which yields an equation for the number fractions

$$w_c f\alpha = w_s(1 - \beta)$$

or the mass fractions

$$m_c = \frac{(1 - \beta)M_c}{\alpha f M_s + (1 - \beta)M_c}$$
$$m_s = \frac{\alpha f M_s}{\alpha f M_s + (1 - \beta)M_c} \tag{11}$$

In these equations M_c and M_s are the molecular weights of the star center and the units of the side chains. The same result could be obtained from eq 6 with the number-average molecular weights for the star center $M_{nc} = M_c$ (homodisperse center) and of the side chains $M_{ns} = M_s/(1 - \beta)$ (side chains with the most probable distribution) and with an average number of side chains $\bar{f} = \alpha f$.

Cascade Substitution

The probability generating functions describe only the chances of reaction between two consecutive generations. For the calculation of overall averages on the macromolecule, the event between all generations have to be joined. This is accomplished by a recurrent cascade substitution of the kind[30-34,41-44,45]

$$U_0 = m_c U_{0c} + m_s U_{0s} \tag{12a}$$

$$\begin{aligned} U_{0c} &= \theta^{\phi_0{}^c}(1 - \alpha + \alpha U_{1,sf})^f \\ U_{0s} &= \theta^{\phi_0{}^s}[1 - \beta + \beta U_{1,sf}][(1 - \beta)U_{1,c} + \beta U_{1,sb}] \end{aligned} \tag{12b}$$

$$\begin{aligned} U_{nc} &= \theta^{\phi_n{}^c}(1 - \alpha + \alpha U_{n+1,sf})^{f-1} \\ U_{nsf} &= \theta^{\phi_n{}^s}(1 - \beta + \beta U_{n+1,sf}) \\ U_{nsb} &= \theta^{\phi_n{}^s}((1 - \beta)U_{n+1,c} + \beta U_{n+1,sb}) \end{aligned} \tag{12c}$$

(Note that the star center can only be linked to a chain with a free end.) The function ϕ_n, which will be specified in the next section, is a weighting factor for a unit in the nth generation (a function of the path length from this unit to the root). The indices c and s indicate the type of unit in the nth generation.

The generating function $U_0(\theta)$ is called the path weighting generating function,[34] which for $\phi_n = 1$ reduces to the weight generating function used previously by Gordon and his coworkers.[32-35]

Molecular and Conformational Averages

On differentiation of eq 12, molecular averages of physical significance are derived. For instance, as was shown previously,[34] with the specifications of eq 13 for ϕ_n one obtains

$$\begin{aligned} &\phi_n = 1 && U_0'(1) = \mathrm{DP_w} \\ &\left.\begin{aligned}\phi_n{}^c &= M_c \\ \phi_n{}^s &= M_s\end{aligned}\right\} && U_0'(1) = M_w \\ &\phi_n = \langle r_n{}^2\rangle && U_0'(1) = 2\mathrm{DP_w}\langle S^2\rangle_z \\ &\phi_n = \exp\left[-\frac{\langle r_n{}^2\rangle}{6}\left(\frac{4\pi}{\lambda}\right)^2 \sin^2 \Theta/2\right] && \\ & && U_0'(1) = \mathrm{DP_w P_z}(\Theta) \end{aligned} \tag{13}$$

where the mean-square end-to-end distance $\langle r_n{}^2\rangle$ between units in the nth generation and the root has to be further specified owing to the fact that both ends can consist of either c or s units. (The type of root is indicated by the second subscript of the two components U_{0c} and U_{0s}, and the other end of the path is indicated by the superscripts of the weighting factors $\phi_n{}^c$ and $\phi_n{}^s$.)

Differentiation of eq 12 yields

$$\begin{aligned} U_{0c}'(1) &= \phi_0{}^c + f\alpha U_{1sf}'(1) \\ U_{0s}'(1) &= \phi_0{}^s + \beta U_{1sf}'(1) + \\ &\qquad (1 - \beta)U_{1c}'(1) + \beta U_{1sb}'(1) \end{aligned} \tag{14a}$$

$$\begin{aligned} U_{nc}'(1) &= \phi_n{}^c + (f - 1)\alpha U_{n+1,sf}'(1) \\ U_{nsf}'(1) &= \phi_n{}^s + \beta U_{n+1,sf}'(1) \\ U_{nsb}'(1) &= \phi_n{}^s + (1 - \beta)U_{n+1,c}'(1) + \beta U_{n+1,sb}'(1) \end{aligned} \tag{14b}$$

These recursion formulas can be replaced by the infinite series

$$U_{0c}'(1) = {}^c\phi_0{}^c + f\alpha \sum_1^\infty \beta^{n-1}({}^c\phi_n{}^s) \tag{15a}$$

$$\begin{aligned} U_{0,s}'(1) = {}^s\phi_0{}^s &+ \\ &2\beta \sum_1^\infty \beta^{n-1}({}^s\phi_n{}^s) + (1 - \beta)\sum_1^\infty \beta^{n-1}({}^s\phi_n{}^c) + \\ &(1 - \beta)(f - 1)\alpha \sum_{k=1}^\infty \beta^{k-1} \sum_{n=1}^\infty \beta^{n-1}({}^s\phi_{n+k}{}^s) \end{aligned} \tag{15b}$$

Two superscripts are now required to unambigiously assign the two ends of a path (left, root; right, the upper end of the path). Equations 15a and 15b comprise all possible paths between a root and any unit in the nth generation.

If the root is a c unit the path can end only with an s unit (eq 15a). Both ends of a path may consist of s units; either both ends belong to the same branch (first two terms in eq 15b) or the ends are in different branches (last term in eq 15b). The latter paths run through the star center and therefore contain one s–c and one c–s link. (The two different branches of these paths are labeled by the suffixes n and k, and the links s–c and c–s are associated with the link probabilities $1 - \beta$ and α, respectively.)

Evidently, with this interpretation of the sums, the mean-square end-to-end distances $\langle r_n{}^2\rangle$ between the root of a tree and units in the nth generation are given by

$$\begin{aligned} {}^c\phi_0{}^c &= 0 \\ {}^c\phi_n{}^s = {}^s\phi_n{}^c &= b_{cs}{}^2 + b_s{}^2(n - 1) \\ {}^s\phi_n{}^s &= b_s{}^2 n \\ {}^s\phi_{n+k}{}^s &= 2b_{cs}{}^2 + b_s{}^2(n - 1) + b_s{}^2(k - 1) \end{aligned} \tag{16}$$

where b_c and b_s are the effective bond lengths between two c units or two s units; the effective bond length between a c and an s unit may be defined by $b_{cs} = ((b_c^2 + b_s^2)/2)^{1/2}$, which corresponds to Gaussian statistics.

Similarly, the weighting factors for calculating the particle scattering factor are

$$\begin{aligned} {}^{c}\phi_0{}^{c} &= 1 \\ {}^{c}\phi_n{}^{s} &= {}^{s}\phi_n{}^{c} = Z_{cs}Z_s{}^{n-1} \\ {}^{s}\phi_n{}^{c} &= Z_s{}^{n} \\ {}^{s}\phi_{n+k}{}^{s} &= [Z_{cs}Z_s{}^{n-1}][Z_{cs}Z_s{}^{k-1}] \end{aligned} \tag{17}$$

where

$$\begin{aligned} Z_c &= \exp(-b_c{}^2h^2/6) \\ Z_{cs} &= \exp(-b_{cs}{}^2h^2/6) \\ Z_s &= \exp(-b_s{}^2h^2/6) \end{aligned} \tag{18}$$

$$h = (4\pi/\lambda)\sin\Theta/2 \tag{19}$$

Inserting the various weighting functions, as defined by eq 13, 16, and 17, into eq 15 the infinite series can be summed with the following final results.

Degree of polymerization

$$\mathrm{DP_w} = 1 + \frac{f\alpha}{1-\beta} + m_s\left[\frac{1+\beta}{1-\beta} - \frac{\alpha}{1-\beta}\right] \tag{20}$$

Molecular weight

$$M_w = M_c + M_s\left[\frac{f\alpha}{1-\beta} + m_s\frac{1+\beta-\alpha}{1-\beta}\right] \tag{21}$$

Mean-square radius of gyration

$$\begin{aligned} \langle S^2\rangle_z = \frac{1}{2\mathrm{DP_w}}\Bigg\{ & m_c\frac{f\alpha}{1-\beta}[b_{cs}{}^2(1-\beta) + b_s{}^2\beta] + \\ & m_s\frac{2\beta}{(1-\beta)^2}b_s{}^2 + m_s\frac{1-\beta+2(f-1)\alpha}{(1-\beta)^2}\times \\ & [b_{cs}{}^2(1-\beta) + b_s{}^2\beta]\Bigg\} \end{aligned} \tag{22}$$

Particle scattering factor

$$\begin{aligned} P_z(\Theta) = \frac{1}{\mathrm{DP_w}}\Bigg\{ & m_c\frac{1-\beta Z_s + f\alpha Z_{cs}}{1-\beta Z_s} + \\ & m_s\left[\frac{1+\beta Z_s}{1-\beta Z_s} + \frac{(1-\beta)Z_{cs}}{1-\beta Z_s} + (1-\beta)\times\right. \\ & \left.(f-1)\alpha\left(\frac{Z_{cs}}{1-\beta Z_s}\right)^2\right]\Bigg\} \end{aligned} \tag{23}$$

The mass fractions are given by eq 11. Equation 20 reduces for $\alpha = 1$ and $M_c = M_s$ ($m_s = w_s$) to a relationship derived previously by Schaefgen and Flory.[46]

Stars with Large Spherical Centers and Grafted Chains Chemically Different from the Center

The equations for the particle scattering factors and the mean-square radii of gyration derived so far are well established approximations for homopolymers built up of small repeat units. This approximation may lead to significant errors, however, for stars in which the weight of the star center deviates considerably from that of a repeat unit of the side chain, where the corresponding refractive indices are different, and where the star center is large and has a diameter of the order of the wavelength of the light used.

The effect of different molecular weights of the two kinds of units becomes clear from the definition of the z average particle scattering factor[47]

$$P_z(\Theta) = \frac{\sum m_xM_xP_x(\Theta)}{\sum m_xM_x} \tag{24}$$

where m_x is the weight fraction of a polymer species of DP $= x$ in the assembly with molecular weight M_x and particle scattering factor $P_x(\Theta)$. Equation 24 only reduces to the usual expression

$$P_z(\Theta) = \frac{\sum m_x x P_x(\Theta)}{\sum m_x x} \tag{25}$$

if, for all components

$$M_x = M_0x \tag{26}$$

For copolymers, however, eq 26 is not valid.[48,49]

One notices that the numerator of eq 24 would become the weight-average molecular weight for $P_x(\Theta) = 1$. This occurs for homopolymers at zero scattering angle and leads to the conclusion that the weighting factors given by eq 16 and 17 have to be multiplied by M_c for ${}^{c}\phi_n{}^{c}$ and ${}^{s}\phi_n{}^{c}$ and by M_s for all the other weighting factors, where M_c and M_s are the molecular weights of the star center and units of the side chains, respectively.

A second correction arises from different refractive index increments of the two types of units. As was shown by Benoit and Wippler[48] the apparent particle scattering factor $P_x(\Theta)$ of a copolymer is given by

$$P_{x,\mathrm{app}}(\Theta) = \frac{1}{x^2\nu^2}\sum_{i=1}^{x}\sum_{j=1}^{x}\nu_i\nu_j\left\langle\frac{\sin hr_{ij}}{hr_{ij}}\right\rangle \tag{27}$$

where ν_i and ν_j are the refractive index increments of the units i and j which form the ends of a path and ν is the average refractive index increment of the total polymer. Since

$$\nu = m_c\nu_c + m_s\nu_s \tag{28}$$

(ν_c and ν_s being respectively the refractive index increments of units c and s) the average value of ν can become zero if

$$m_c\nu_c = -m_s\nu_s$$

and this may happen for nonzero values of ν_c and ν_s. Thus, $P_{x,\mathrm{app}}(\Theta)$ in general does not become unity at zero angle but can have a considerably higher value. Due to this effect the apparent molecular weight

$$M_{w,\mathrm{app}} = \lim_{\Theta\to 0}\sum m_xM_xP_{x,\mathrm{app}}(\Theta) \tag{29}$$

may be also considerably higher than the true M_w,[49] because of eq 27

$$P_{x,\mathrm{app}}(0) = \frac{1}{x^2\nu^2}\sum_{i=1}^{x}\sum_{j=1}^{x}\nu_i\nu_j \neq 1 \tag{27'}$$

This effect can easily be accounted for in the cascade theory. Since ν_i and ν_j occur only at the ends of a path (eq. 27) one has to multiply the weighting factors ${}^{c}\phi_n{}^{c}$ by $g_c{}^2$, ${}^{c}\phi_n{}^{s}$ by g_cg_s, and ${}^{s}\phi_n{}^{s}$ by $g_s{}^2$, where $g_c = \nu_c/\nu$ and $g_s = \nu_s/\nu$.

The third correction to be applied has its origin in large centers, since these cause additional interference effects. Such cases are common for X-ray small-angle scattering but certainly rare for visible light.

An exception occurs if chains are grafted onto the surface of latex particles or suitable microgels. Here one has to make use of the full definition of the particle scattering factor of a molecule which reads[50]

$$P_x(\Theta) = \frac{1}{x^2} \sum_{i=1}^{x} \sum_{j=1}^{x} f_i f_j \left\langle \frac{\sin hr_{ij}}{hr_{ij}} \right\rangle \tag{30}$$

where f_i and f_j are the so called structure factors of the repeat units i and j. The structure factors are related to the particle scattering factors $P_{0i}(\Theta)$ of the repeat unit through

$$f_i^{\,2} = P_{0i}(\Theta) \tag{31}$$

Since $P_{0i}(\Theta)$ can be well represented by the Guinier approximation[51,52]

$$P_{0i}(\Theta) \approx \exp(-h^2\langle S^2\rangle_{0i}/3) \tag{32}$$

the structure factor is

$$f_i \approx \exp(-h^2\langle S^2\rangle_{0i}/6) \tag{33}$$

where $\langle S^2 \rangle_{0i}$ is the mean-square radius of gyration of the ith repeat unit. Formally eq 30 is identical with eq 27, and thus the required corrections are of the same type and are performed by multiplying ${}^{\rm c}\phi_n{}^{\rm c}$ by $f_{\rm c}{}^2$ and ${}^{\rm s}\phi_n{}^{\rm c}$ by $f_{\rm c}f_{\rm s}$ and ${}^{\rm s}\phi_n{}^{\rm s}$ by $f_{\rm s}{}^2$.

Combining the three corrections described above one obtains for the weighting factors for the particle scattering factor

$$\begin{aligned}
{}^{\rm c}\phi_n{}^{\rm c} &= M_{\rm c}g_{\rm c}{}^2 f_{\rm c}{}^2 Z_{\rm c}{}^n \\
{}^{\rm c}\phi_n{}^{\rm s} &= M_{\rm s}g_{\rm c}\, g_{\rm s} f_{\rm c} f_{\rm s} Z_{\rm cs} Z_{\rm s}{}^{n-1} \\
{}^{\rm s}\phi_n{}^{\rm c} &= M_{\rm c}g_{\rm c}\, g_{\rm s} f_{\rm c} f_{\rm s} Z_{\rm cs} Z_{\rm s}{}^{n-1} \\
{}^{\rm s}\phi_n{}^{\rm s} &= M_{\rm s}\, g_{\rm s}{}^2 f_{\rm s}{}^2 Z_{\rm s}{}^n \\
{}^{\rm s}\phi_{n+k}{}^{\rm s} &= M_{\rm s}\, g_{\rm s}{}^2 f_{\rm s}{}^2 [Z_{\rm cs} Z_{\rm s}{}^{n-1}][Z_{\rm cs} Z_{\rm s}{}^{k-1}]
\end{aligned} \tag{34}$$

The mean-square radius of gyration follows from the series expansion of

$$P_{x,\,\rm app}(\Theta) = \frac{1}{x^2}\sum\sum g_i f_i g_j f_j \left\langle \frac{\sin hr_{ij}}{hr_{ij}} \right\rangle \tag{35}$$

which reads

$$\begin{aligned}
P_{x,\,\rm app}(\Theta) &= \frac{1}{x^2}\sum\sum g_i g_j - \frac{h^2}{6}\,\frac{1}{x^2}\sum\sum g_i g_j\,[\langle r_{ij}{}^2\rangle + \\
&\qquad \langle S^2\rangle_{0i} + \langle S^2\rangle_{0j}] + \ldots \\
&= \frac{1}{x^2}\sum\sum g_i g_j \left(1 - \frac{h^2}{3}\, \langle S^2\rangle_{x,\,\rm app}\right) + \ldots
\end{aligned}$$

Thus

$$\langle S^2\rangle_{x,\,\rm app}\left(\frac{1}{x^2}\sum\sum g_i g_j\right) = \frac{1}{2x^2}\sum\sum g_i g_j [\langle r_{ij}{}^2\rangle + \langle S^2\rangle_{0i} + \langle S^2\rangle_{0j}]$$

This means that at each end of a path (i, j) the mean-square radii of gyration of the corresponding repeat units have to be added. From this one finds the weighting factors of the apparent mean-square radius of gyration (*cf.* eq 16)

$$\begin{aligned}
{}^{\rm c}\phi_0{}^{\rm c} &= M_{\rm c}g_{\rm c}{}^2 2\langle S^2\rangle_{0\rm c} \\
{}^{\rm c}\phi_n{}^{\rm s} &= M_{\rm s}g_{\rm c}g_{\rm s}[b_{\rm cs}{}^2 + b_{\rm s}{}^2(n-1) + \langle S^2\rangle_{0\rm c} + \langle S^2\rangle_{0\rm s}] \\
{}^{\rm s}\phi_n{}^{\rm c} &= M_{\rm c}g_{\rm c}g_{\rm s}[b_{\rm cs}{}^2 + b_{\rm s}{}^2(n-1) + \langle S^2\rangle_{0\rm c} + \langle S^2\rangle_{0\rm s}] \\
{}^{\rm s}\phi_n{}^{\rm s} &= M_{\rm s}g_{\rm s}{}^2[b_{\rm s}{}^2 n + 2\langle S^2\rangle_{0\rm s}] \\
{}^{\rm s}\phi_{n+k}{}^{\rm s} &= M_{\rm s}g_{\rm s}{}^2[2b_{\rm cs}{}^2 + b_{\rm s}{}^2(n-1+k-1) + 2\langle S^2\rangle_{0\rm s}]
\end{aligned} \tag{36}$$

Insertion of eq 33 into eq 15 yields for the apparent z-average particle scattering factor

$$\begin{aligned}
P_{z,\,\rm app}(\Theta)M_{\rm w} &= m_{\rm c}\left[M_{\rm c}g_{\rm c}{}^2 f_{\rm c}{}^2 + M_{\rm s}g_{\rm s}g_{\rm c}f_{\rm s}f_{\rm c}\frac{\alpha f Z_{\rm cs}}{1-\beta Z_{\rm s}}\right] + \\
&\quad m_{\rm s}\left[M_{\rm s}g_{\rm s}{}^2 f_{\rm s}{}^2\frac{1+\beta Z_{\rm s}}{1-\beta Z_{\rm s}} + M_{\rm c}g_{\rm c}g_{\rm s}f_{\rm c}f_{\rm s}\frac{(1-\beta)Z_{\rm cs}}{1-\beta Z_{\rm s}} + \right. \\
&\qquad \left. M_{\rm s}g_{\rm s}{}^2 f_{\rm s}{}^2(1-\beta)(f-1)\alpha\left(\frac{Z_{\rm sc}}{1-\beta Z_{\rm s}}\right)^2\right]
\end{aligned} \tag{37}$$

The apparent molecular weight follows from eq 37 by setting $Z_{\rm c} = 1$, $Z_{\rm s} = 1$, and $Z_{\rm cs} = 1$ and also $f_{\rm c} = f_{\rm s} = 1$

$$\begin{aligned}
M_{\rm w,\,app} &= m_{\rm c}\left[M_{\rm c}g_{\rm c}{}^2 + M_{\rm s}g_{\rm s}g_{\rm c}\frac{\alpha f}{1-\beta}\right] + \\
&\qquad m_{\rm s}\left[M_{\rm s}g_{\rm s}{}^2\frac{1+\beta+(f-1)\alpha}{1-\beta} + M_{\rm c}g_{\rm c}g_{\rm s}\right]
\end{aligned} \tag{38}$$

The apparent mean-square radius of gyration is obtained by inserting eq 36 into eq 15. The passage from apparent to true values of $M_{\rm w}$, $\langle S^2 \rangle_{\rm z}$, and $P_{\rm z}$ will be discussed in part II.

$$\begin{aligned}
\langle S^2\rangle_{z,\,\rm app}M_{\rm app} &= \frac{1}{2}\left\{m_{\rm c}M_{\rm s}g_{\rm c}g_{\rm s}\frac{f\alpha}{1-\beta}G_1 + \right. \\
&\quad m_{\rm s}\left[M_{\rm s}g_{\rm s}{}^2\frac{2}{1-\beta}G_2 + M_{\rm c}g_{\rm c}g_{\rm s}G_1\right] + \\
&\quad m_{\rm c}\left[M_{\rm c}g_{\rm c}{}^2 2\langle S^2\rangle_{0\rm c} + M_{\rm s}g_{\rm s}g_{\rm c}\frac{\alpha f}{1-\beta}(\langle S^2\rangle_{0\rm c} + \langle S^2\rangle_{0\rm s})\right] + \\
&\quad m_{\rm s}\left[M_{\rm s}g_{\rm s}{}^2\frac{1+\beta+(f-1)\alpha}{1-f}2\langle S^2\rangle_{0\rm s} + \right. \\
&\qquad \left.\left. M_{\rm c}g_{\rm c}g_{\rm s}(\langle S^2\rangle_{0\rm c} + \langle S^2\rangle_{0\rm s})\right]\right\}
\end{aligned} \tag{39}$$

where

$$\begin{aligned}
G_1 &= \frac{b_{\rm cs}{}^2(1-\beta) + b_{\rm s}\beta}{1-\beta} \\
G_2 &= \frac{\beta}{1-\beta}b_{\rm s}{}^2 + (f-1)\alpha G_1
\end{aligned} \tag{39a}$$

Stiff Side Chains

An approximate solution of the effect of stiff chains on the mean-square radius of gyration and the particle scattering factor can be derived if the chain stiffness is restricted to the side chains, while the joints to the star center are considered to be flexible links. On these assumptions the only change necessary is to substitute the end-to-end distance function $\langle r_n{}^2 \rangle$ for stiff chains and the corresponding Fourier transform of the distance distribution $\langle \sin hr_n/hr_n \rangle$ into the weighting factors.

The Fourier transform for a Porod wormlike chain[53] was calculated by Daniels to a second-order approximation and may be written as[54,55]

$$\left\langle \frac{\sin hr_n}{hr_n} \right\rangle_{\mathrm{s}} = (1 + C_{p_1}X^2)Z_{\mathrm{s}}^{\,n} + C_{p_2}\frac{\partial}{\partial X^2}(Z_{\mathrm{s}}^{\,n}) \tag{40}$$

where

$$X^2 = \frac{1 + \cos \gamma}{1 - \cos \gamma}h^2b_{\mathrm{s}}^{\,2} = \frac{2 - q}{q}h^2b_{\mathrm{s}}^{\,2}$$

$$q = 1 - \cos \gamma$$

$$Z_{\mathrm{s}} = \exp(-X^2/6) \tag{41}$$

and

$$C_{p_1} = \frac{1}{3}\frac{1 - q}{q}$$

$$C_{p_2} = -\frac{1}{15q(2 - q)}\left[-\frac{1}{2}(10 - 10 + 3q^2) + \frac{1}{3}(4 - 6q + 3q^2)\right] \tag{42}$$

In these equations γ is the complementary apparent valence angle between two consecutive bonds. The parameter q is related to the persistence length a and the bond length b_{s} through

$$1/q = a/b_{\mathrm{s}} \tag{43}$$

and is a useful stiffness parameter, since a/b_{s} represents the number of bonds per persistence length.

Instead of the set of eq 33 the following weighting factors have to be used in calculating the particle scattering factor

$$\begin{aligned}
{}^{\mathrm{c}}\phi_0^{\,\mathrm{c}} &= M_{\mathrm{c}}g_{\mathrm{c}}^{\,2}f_{\mathrm{c}}^{\,2} \\
{}^{\mathrm{c}}\phi_n^{\,\mathrm{s}} &= M_{\mathrm{s}}g_{\mathrm{s}}g_{\mathrm{c}}f_{\mathrm{s}}f_{\mathrm{c}}Z_{\mathrm{cs}}\left[(1 + C_{p_1}X^2)Z_{\mathrm{s}}^{\,n-1} + C_{p_2}\frac{\partial}{\partial X^2}Z_{\mathrm{s}}^{\,n-1}\right] \\
{}^{\mathrm{s}}\phi_n^{\,\mathrm{c}} &= M_{\mathrm{c}}g_{\mathrm{s}}g_{\mathrm{c}}f_{\mathrm{s}}f_{\mathrm{c}}Z_{\mathrm{cs}}\left[(1 + C_{r_1}X^2)Z_{\mathrm{s}}^{\,n-1} + C_{p_2}\frac{\partial}{\partial X^2}Z_{\mathrm{s}}^{\,n-1}\right] \\
{}^{\mathrm{s}}\phi_n^{\,\mathrm{s}} &= M_{\mathrm{s}}g_{\mathrm{s}}^{\,2}f_{\mathrm{s}}^{\,2}\left[(1 + C_{p_1}X^2)Z_{\mathrm{s}}^{\,n} + C_{p_2}\frac{\partial}{\partial X^2}Z_{\mathrm{s}}^{\,n}\right] \\
{}^{\mathrm{s}}\phi_{n+k}^{\,\mathrm{s}} &= M_{\mathrm{s}}g_{\mathrm{s}}^{\,2}f_{\mathrm{s}}^{\,2}Z_{\mathrm{cs}}^{\,2}\left[(1 + C_{p_1}X^2)Z_{\mathrm{s}}^{\,n-1} + C_{p_2}\frac{\partial}{\partial X^2}Z_{\mathrm{s}}^{\,n-1}\right]\left[(1 + C_{p_1}X^2)Z_{\mathrm{s}}^{\,k-1} + C_{p_2}\frac{\partial}{\partial X^2}Z_{\mathrm{s}}^{\,k-1}\right]
\end{aligned} \tag{44}$$

After insertion in eq 15a and 15b the result may be summarized as

$$P_{\mathrm{z,app}}(\Theta)M_{\mathrm{w}} = m_{\mathrm{c}}[M_{\mathrm{c}}g_{\mathrm{c}}^{\,2}f_{\mathrm{c}}^{\,2} + M_{\mathrm{s}}g_{\mathrm{s}}g_{\mathrm{c}}f_{\mathrm{s}}f_{\mathrm{c}}\alpha fY_1] + m_{\mathrm{s}}[M_{\mathrm{s}}g_{\mathrm{s}}^{\,2}f_{\mathrm{s}}^{\,2}Y_2 + M_{\mathrm{c}}g_{\mathrm{c}}g_{\mathrm{s}}f_{\mathrm{c}}f_{\mathrm{s}}(1 - \beta)Y_1 + M_{\mathrm{s}}g_{\mathrm{s}}^{\,2}f_{\mathrm{s}}^{\,2}(1 - \beta)(f - 1)\alpha Y_1^{\,2}] \tag{45}$$

where

$$Y_1 = Z_{\mathrm{cs}}\left[\frac{1 + C_{p_1}X^2}{1 - \beta Z_{\mathrm{s}}} - \frac{C_{p_2}}{6}\frac{\beta Z_{\mathrm{s}}}{(1 - \beta Z_{\mathrm{s}})^2}\right]$$

$$Y_2 = \left[(1 + C_{p_1}X^2)\frac{1 + \beta Z_{\mathrm{s}}}{1 - \beta Z_{\mathrm{s}}} - \frac{C_{p_2}}{3}\frac{\beta Z_{\mathrm{s}}}{(1 - \beta Z_{\mathrm{s}})^2}\right] \tag{46}$$

The mean-square end-to-end distance between two arbitrary repeat units of a stiff chain with freely rotating units is known exactly[56] and can be rewritten in terms of the effective bond length $b_{\mathrm{eff,s}}$ and the stiffness parameter q

$$\langle r_n^{\,2}\rangle_{\mathrm{s}} = b_{\mathrm{eff,s}}^{\,2}\{n - 2C_1[1 - (1 - q)^n]\} \tag{47}$$

where

$$b_{\mathrm{eff,s}}^{\,2} = b_{\mathrm{s}}^{\,2}\frac{2 - q}{q} \tag{48}$$

$$C_1 = \frac{1 - q}{(2 - q)q} \tag{49}$$

The index s indicates that only side chains are considered. Correspondingly, for the mean-square radius of gyration of stars with stiff side chains but flexible joints to the center, the weighting factors are

$$\begin{aligned}
{}^{\mathrm{s}}\phi_0^{\,\mathrm{s}} &= M_{\mathrm{c}}g_{\mathrm{c}}^{\,2}2\langle S^2\rangle_{0\mathrm{c}} \\
{}^{\mathrm{c}}\phi_n^{\,\mathrm{s}} &= M_{\mathrm{s}}g_{\mathrm{s}}g_{\mathrm{c}}[b_{\mathrm{cs}}^{\,2} + \langle r_{n-1}^{\,2}\rangle_{\mathrm{s}} + \langle S^2\rangle_{0\mathrm{c}} + \langle S^2\rangle_{0\mathrm{s}}] \\
{}^{\mathrm{s}}\phi_n^{\,\mathrm{c}} &= M_{\mathrm{c}}g_{\mathrm{c}}g_{\mathrm{s}}[b_{\mathrm{cs}} + \langle r_{n-1}^{\,2}\rangle_{\mathrm{s}} + \langle S\rangle_{0\mathrm{c}} + \langle S\rangle_{0\mathrm{s}}] \\
{}^{\mathrm{s}}\phi_n^{\,\mathrm{s}} &= M_{\mathrm{s}}g_{\mathrm{s}}^{\,2}[\langle r_n^{\,2}\rangle_{\mathrm{s}} + 2\langle S\rangle_{0\mathrm{s}}] \\
{}^{\mathrm{s}}\phi_{n+k}^{\,\mathrm{s}} &= M_{\mathrm{s}}g_{\mathrm{s}}^{\,2}[2b_{\mathrm{cs}}^{\,2} + \langle r_{n-1}^{\,2}\rangle_{\mathrm{s}} + \langle r_{k-1}^{\,2}\rangle_{\mathrm{s}} + 2\langle S\rangle_{0\mathrm{s}}]
\end{aligned} \tag{50}$$

Inserting eq 50 into eq 15a and 15b the following result for the apparent mean-square radius of gyration is obtained

$$\langle S^2\rangle_{\mathrm{z,app}} = \langle S^2\rangle_{\mathrm{z,app}}^{\mathrm{Ganss}} - \langle S^2\rangle_{\mathrm{z,app}}^{\mathrm{non\text{-}Ganss}} \tag{51}$$

where $\langle S^2\rangle_{\mathrm{z,app}}^{\mathrm{Gauss}}$ is given by eq 39 when $b_{\mathrm{s}}^{\,2}$ is replaced by $b_{\mathrm{eff,s}}^{\,2}$; the correction term is

$$\langle S^2\rangle_{\mathrm{z,app}}^{\mathrm{non\text{-}Gauss}} = \frac{b_{\mathrm{eff,s}}^{\,2}}{M_{\mathrm{w,app}}}\frac{C_1\beta q}{1 - \beta(1 - q)}\left[m_{\mathrm{c}}M_{\mathrm{s}}g_{\mathrm{c}}g_{\mathrm{s}}\frac{\alpha f}{1 - \beta} + 2m_{\mathrm{s}}M_{\mathrm{s}}g_{\mathrm{s}}^{\,2}\frac{1 + (f - 1)\alpha}{1 - \beta} + m_{\mathrm{s}}M_{\mathrm{c}}g_{\mathrm{c}}g_{\mathrm{s}}\right] \tag{52}$$

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(43) (a) Equation 10 has a simple meaning. As can easily be verified, the partial differential quotient $(\partial F_{0c}/\phi\theta_s)_{\theta=1}$ gives the average number of s units linked to a star center and correspondingly $(\partial F_{0s}/\partial\theta_c)_{\theta=1}$ is the number of star centers linked on the average to an s unit. Therefore eq 10 states the trivial mass conservation condition that the total number of s units linked to star centers equals the total number of star centers which are linked to s units. (b) In a completely random process $F_n(\theta)$ ($n > 0$) can also be derived from $F_0(\theta)$ through Gordon's theorem. However, this theorem is not applicable to chains with correlation between the link probabilities of units which are separated by more than two generations (second shell substitution effect). The attached side chains of the star molecules imply a particular long-range correlation between the link probabilities, because a repeating unit from a free end branch can be linked only to another unit from that branch but not with one from the bound end branch. Such a correlation is characteristic for chain processes where the reaction can proceed only in one direction.
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Statistics of Star-Shaped Molecules. II. Stars with Homodisperse Side Chains

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ABSTRACT: The cascade theory, known to be a powerful method when dealing with random processes, has been extended to cover the problem of copolymeric star molecules with side chains of equal length. This has been effected by introducing a special form of correlation between probabilities in the zeroth and nth generations. Analytic formulas are derived for the apparent and true values of the weight-average molecular weight and the z averages of the mean-square radius of gyration and the particle scattering factor. The particle scattering factors exhibit characteristic upturns in Zimm plots; the upturn is increased with the number of side chains and is more pronounced for homodisperse side chains than for side chains with a random length distribution. The envelopes of the particle scattering factors show increasingly marked downturns at large angles of scatter for stiff chains, resulting in typical S-shaped curves in Zimm plots. Particular attention is given to the apparent and true averages of the molecular weight and of the conformation of copolymeric stars. The results are expressed in terms of heterogeneity parameters P and Q defined by Benoit and Froelich for block copolymers. For star molecules Q is shown to be a simple function of P and the mass fraction of the star center, while P depends on the difference between the weight- and number-average molecular weight.

The star molecules considered in the preceding paper (part I) are characterized by a most probable length distribution for the attached side chains. In this paper the case of homodisperse side chains is treated. Although this problem was solved approximately by Benoit,[1] more general relationships can be obtained by an extension of the existing cascade theory. To make this intelligible a characteristic and slightly hidden correlation between the link probabilities in star molecules may be discussed in some detail.

In the previous case of stars with most probable length distribution for the side chains three link probabilities had to be distinguished for the side chains: (i) the probability β that an s unit of the side chain is linked to another s unit of the same chain, (ii) the probability $(1 - \beta)$ that a functionality of the s unit is not linked, and (iii) the probability $(1 - \beta)p_c$ that the s unit is linked to a unit c of the star center, where for the coupling probability $p_c = 1$ has been assumed. More generally one has $p_c < 1$, and in such a case $(1 - \beta)(1 - p_c)$ indicates the probability that a fraction of $(1 - p_c)$ of all linear s chains is not linked to the center. The fact that the one end of the side chain is attached to the center while the other is free implies a special correlation between the link probabilities. In a completely random process the two functionalities of a bifunctional unit are indistinguishable. In this case, however, the functionality facing the free end has the chance β for a link and $(1 - \beta)$ for no reaction, and the same situation holds for any other generation of the branch that leads to the free end; the functionality facing the attached end, on the other hand, has again the probability β for a link to another s unit, but the alternative is now $(1 - \beta)p_c$ for the link probability with a unit of the star center, and the same situation persists for all higher generations of that attached branch. This type of correlation, which is also typical for the chain process of a free radical polymerization, has been accounted for in part I by a special labeling of the generating functions. Yet, the probabilities remain identical in all generations; in other words β has been assumed to be independent of the number of s units between the center and an s unit selected at random.