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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.

For strictly or nearly homodisperse side chains (*e.g.*, Poisson distribution) such an independence does not exist. Here it is more effective to replace the link probabilities by fixed values (no fluctuation). If for these molecules a unit is chosen at random to furnish a root of a tree, a forest is again obtained with subforests of c-rooted and s-rooted trees (for an explanation of various terms and symbols used, see part I). However, the various s-rooted trees are not statistically equivalent but depend on whether the first unit nearest to the star center, or the end unit of the side chain, or say the ith s unit, counted from the center, is the root. Again this strong correlation can be handled by labeling the various generating functions. This leads to the following generalization of the path-weighting generating functions.

The Generating Function

As before, the component for the star center is

$$U_{0c} = \theta^{\Phi_0{}^c}(1 - \alpha + \alpha U_{1sf}{}^N)^f \tag{1}$$

where the superscript (*not* a power index) N denotes the fact that a side chain of N units in length is affixed to the center with a probability α.

For the s-rooted trees the generating function is now a weighted sum of individual generating functions

$$U_{0s} = \frac{1}{N}\sum_{i=1}^{N} U_{0s}{}^i \tag{2}$$

where the average is taken over the N different s-rooted trees with individual generating functions

$$U_{0s}{}^i = \theta^{\Phi_0{}^s} U_{1sf}{}^{N-i} U_{1sb}{}^{i-1} \tag{3}$$

Here the index i in $U_{0s}{}^i$ means that the ith s unit (counted from the star center) is the root of the tree. $U_{1sf}{}^{N-i}$ and $U_{1sb}{}^{i-1}$ are respectively the generating functions for the first generation of branches with a free end and the end bound to the center. Evidently, if the ith unit is a root, there are $N - i$ units on the branch with the free end and $i - 1$ units on the branch bearing the star center.

For the first and the subsequent generations one finds for the c component

$$U_{ic} = \theta^{\Phi_i{}^c}(1 - \alpha + \alpha U_{i+1,sf}{}^N)^{f-1} \tag{4}$$

For the two parts of the side chain one has the series

$$\begin{aligned} U_{1sf}{}^{N-i} &= \theta^{\Phi_1{}^s} U_{2sf}{}^{N-i-1} \\ U_{jsf}{}^{N-i-j+1} &= \theta^{\Phi_j{}^s} U_{j+1,sf}{}^{N-i-j} \\ &\qquad (j = 2, 3, \ldots, N - i - 1) \\ U_{N-i}{}^1 &= \theta^{\Phi_{N-i}{}^s} \end{aligned} \tag{5}$$

and

$$\begin{aligned} U_{1sb}{}^{i-1} &= \theta^{\Phi_1{}^s} U_{2sb}{}^{i-2} \\ U_{jsb}{}^{i-j} &= \theta^{\Phi_j{}^s} U_{j+1,sb}{}^{i-j-1} \\ &\qquad (j = 2, 3, \ldots, i - 2) \\ U_{i-1,sb}{}^1 &= \theta^{\Phi_{i-1}{}^s} U_{ic} \end{aligned} \tag{6}$$

Both recursions are readily solved, thus

$$U_{1sf}{}^{N-i} = \prod_{j=1}^{N-i} \theta^{\Phi_j{}^s} \tag{7}$$

$$U_{1sb}{}^{i-1} = \prod_{j=1}^{i-1} \theta^{\Phi_j{}^s} U_{ic} \tag{8}$$

Combination of the eq 1–4, 7, and 8 yields

$$U_{0c} = \theta^{\Phi_0{}^c}(1 - \alpha + \alpha \prod_{j=1}^{N} \theta^{\Phi_j{}^s})^f \tag{9}$$

$$U_{0s} = \theta^{\Phi_0{}^s} \frac{1}{N}\sum_{i=1}^{N} [\theta^{\Phi_i{}^c}(1 - \alpha + \alpha \prod_{l=1}^{N} \theta^{\Phi_{i+l}{}^s})^{f-1}(\prod_{j=1}^{N-i} \theta^{\Phi_j{}^s})(\prod_{k=1}^{i-1} \theta^{\Phi_k{}^s})] \tag{10}$$

Again two superscripts are used in order to label clearly both ends of a path.

The total path-weighting generating function is

$$U_0 = m_c U_{0c} + m_s U_{0s} \tag{11}$$

The mass fractions m_c and m_s follow from eq 6b of part I by insertion of $M_{nc} = M_c$ and $M_{ns} = NM_s$ as the number-average molecular weights of the center and of a side chain, respectively, and the average number $\bar{f} = \alpha f$ of side chains

$$m_c = \frac{M_c}{M_c + \alpha f N M_s}; \quad m_s = \frac{\alpha f N M_s}{M_c + \alpha f N M_s} \tag{12}$$

The relevant physical averages are obtained from eq 11 by differentiation at $\theta = 1$, resulting in

$$U_0'(1) = m_c\left[{}^c\phi_0{}^c + f\alpha\sum_{j=1}^{N} {}^c\phi_j{}^s\right] + m_s\left[{}^s\phi_0{}^s + \frac{1}{N}\sum {}^s\phi_i{}^c + \frac{2}{N}\sum_{i=1}^{N-1}(N - i){}^s\phi_i{}^s + \frac{1}{N}\sum_{i=1}^{N}(f - 1)\alpha\sum_{l=1}^{N} {}^s\phi_{i+l}{}^s\right] \tag{13}$$

Gaussian Chains

The z average of the apparent particle scattering factor follows from the set of weighting functions defined in eq 33 or Part I (unless otherwise mentioned, all the equation numbers refer to this paper). If these functions are inserted in eq 13, one obtains

$$P_{z,app}(\Theta)M_w = m_c\{M_c g_c{}^2 f_c{}^2 + M_s g_s g_c f_s f_c \alpha f P_1\} + m_s\left\{M_s g_s{}^2 f_s{}^2\left[P_2 + \frac{(f - 1)\alpha}{N} P_1{}^2\right] + M_c g_c g_s f_c f_s \frac{P_1}{N}\right\} \tag{14}$$

where

$$\begin{aligned} P_1 &= Z_{cs}[(1 - Z_s{}^N)/(1 - Z_s)] \\ P_2 &= 1 + \frac{2Z_s}{1 - Z_s}\left(1 - \frac{P_1}{NZ_{cs}}\right) \end{aligned} \tag{15}$$

The apparent molecular weight is found from the limit $\Theta \to 1$ of eq 15; this limit is equivalent to $Z_{cs} \to 1$ and $Z_s \to 1$ and, with these limiting operations, both P_1 and $P_2 \to N$. Thus

$$M_{w,app} = m_c\{M_c g_c{}^2 + M_s g_s g_c \alpha f N\} + m_s\{M_s g_s{}^2[\alpha f N + (1 - \alpha)N] + M_c g_c g_s\} \tag{16}$$

Insertion of eq 36 of I in eq 13 gives the z average of the mean-square radius of gyration:

$$\langle S^2\rangle_{z,app} = \frac{1}{2M_{w,app}}\{m_c M_s g_c g_s \alpha f N G_{10} + m_s[M_c g_c g_s G_{10} + M_s g_s^2 G_{20}] + m_c[M_c g_c^2 2\langle S^2\rangle_{0c} + M_s g_s g_c \alpha f N(\langle S^2\rangle_{0c} + \langle S^2\rangle_{0s})] + m_s[M_s g_s^2 2\langle S^2\rangle_{0s}(\alpha f N + (1-\alpha)N + M_c g_s g_c(\langle S^2\rangle_{0c} + \langle S^2\rangle_{0s})]\} \quad (17)$$

where

$$G_{10} = b_{cs}^2 + [(N-1)/2]b_s^2$$

$$G_{20} = \frac{(N-1)(N+1)}{3} b_s^2 + 2(f-1)\alpha N G_{10} \quad (18)$$

Stiff Side Chains

An equation for the apparent particle scattering factor is obtained now with the set of eq 44 of I

$$P_{z,app}(\Theta)M_w = m_c[M_c g_c^2 f_c^2 + M_s g_s g_c f_s f_c \alpha f Y_{10}] + M_s\left[M_s g_s^2 f_s^2\left(Y_{20} + \frac{(f-1)\alpha}{N} Y_{10}^2\right) + M_c g_c g_s f_c f_s \frac{Y_{10}}{N}\right] \quad (19)$$

where

$$Y_{10} = Z_{cs}\left[(1 + C_{p_1}X^2)\frac{P_1}{Z_{cs}} - \frac{C_{p_2}}{6}\frac{Z_s(1-Z_s^N) - N(1-Z_s)Z_s^N}{(1-Z_s^N)^2}\right]$$

$$Y_{20} = (1 + C_{p_1}X^2)P_2 - \frac{C_{p_2}}{3}\frac{Z_s}{(1-Z_s)^2}\left[(1+Z_s)\frac{P_1}{Z_{cs}N} - (1+Z_s^N)\right] \quad (20)$$

The functions X^2 and Z_s are given by eq 41 of I, C_{p_1} and C_{p_2} by eq 42 of I, and P_1 and P_2 by eq 15; the other symbols have the same meaning as before.

Finally, for the apparent mean-square radius of gyration, one finds from eq 50 of I and eq 13

$$\langle S^2\rangle_{z,app} = \langle S^2\rangle_{z,app}^{Gauss} - \langle S^2\rangle_{z,app}^{non\text{-}Gauss} \quad (21)$$

The first term is given by eq 17 and the correction term is

$$\langle S^2\rangle_{z,app}^{non\text{-}Gauss} = \frac{b_{eff,s}^2}{2M_{w,app}} C_1\left\{m_c M_s g_s g_c H_1 + m_s M_c g_s g_c \frac{H_1}{N} + 2m_s M_s g_s^2\left[H_2 + \frac{(f-1)\alpha}{N} H_1\right]\right\} \quad (22)$$

with

$$H_1 = (N-1) - \frac{1-(1-q)^N}{q}$$

$$H_2 = (N-1) - \frac{1-q}{q}\left[1 - \frac{1-(1-q)^N}{Nq}\right] \quad (23)$$

The constant C_1 is defined in eq 49 of I.

Results and Discussion

A few conclusions from the results obtained in I and in the preceding sections of this paper are discussed here.

Effect of the Chain Number, Chain Length Distribution, and Chain Stiffness. Figure 1 shows the reciprocal particle scattering factors as a function of $h^2\langle S^2\rangle_z$ for some stars with point centers. All particle scattering factors

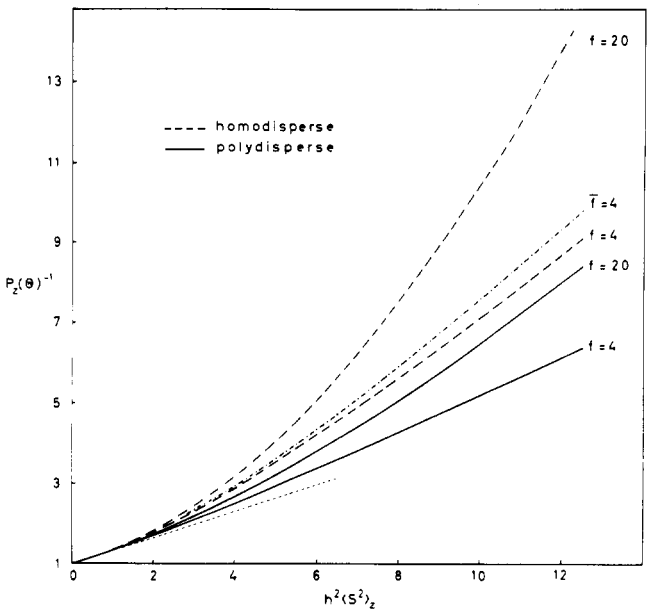

Figure 1. Reciprocal particle scattering factors of star molecules with 4 and 20 branches, respectively. The broken lines refer to homodisperse branches and the solid ones to branches with most probable length distribution. Curve $\bar{f} = 4$ represents behavior of an assembly of stars with a maximum number of 20 branches but an average of 4 branches.

exhibit the same initial slope of ⅓; an upturn at large values of the abscissa is more pronounced for stars with homodisperse side chains than for side chains with a most-probable length distribution. A similar relationship is found for homodisperse linear polymers and for those with the most-probable distribution, although in this case the upturns are rather less pronounced. The upturn is also enhanced by increase of the number of side chains. This behavior is typical of the effect of branching but is often superimposed on an opposite effect due to polydispersity.[2-4]

The curves with an average number $\bar{f} = \alpha f = 4$ are of special interest. Here the functionality is $f = 20$ but only 20% of the reactive groups of the center have reacted. The particle scattering factor shows behavior similar to that of a star with exactly four side chains, but is not identical with it because of the variation in chain number of different stars in the assembly. This observation suggests a test for uniform grafting.

The effect of chain stiffness is seen in Figure 2 for the example of stars with 20 side chains. The chain stiffness is characterized by the parameter $1/q$ which indicates the number of repeat units per persistence length. While for Gaussian chains ($1/q = 1$) a continuous upturn is observed, the corresponding particle scattering factors of stiffer chains show the typical downturn behavior of stiff chains in general.[5-7] As long as the chain stiffness is not too high, a characteristic S shaped curve is obtained, as confirmed experimentally.[8] In such cases an easy determination of the chain stiffness will be possible; for chains with more than 100 bonds per persistence length, however, the downturn due to chain stiffness sets in so early that difficulties of interpretation similar to those for stiff linear chains[5-7] will occur.

Copolymeric Stars. If the star center is comparable in size and mass with the mean-square radius of gyration of a side chain and the total mass of all grafted side chains, the star has to be considered as a copolymer, especially if the center (microgel or latex particle) and the side chains have different refractive index increments.

Figure 3 shows the influence of the refractive index in-

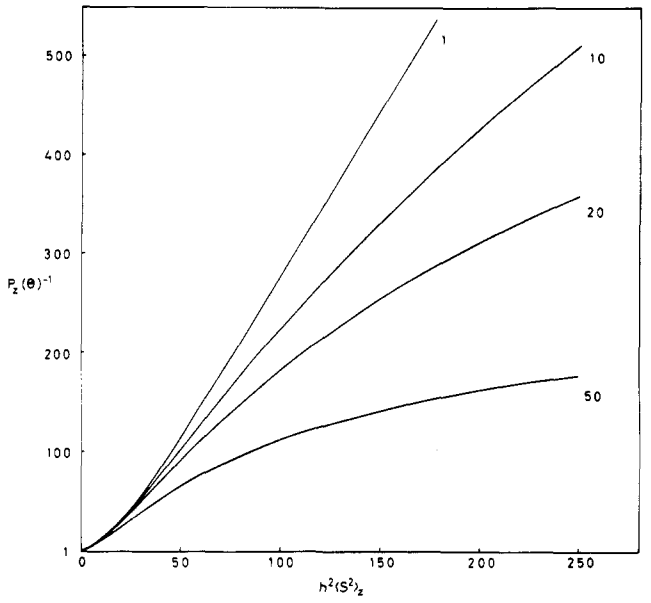

Figure 2. Effect of chain stiffness on the reciprocal particle scattering factors of star molecules bearing 20 branches. The figures denote the number of repeat units per persistence length.

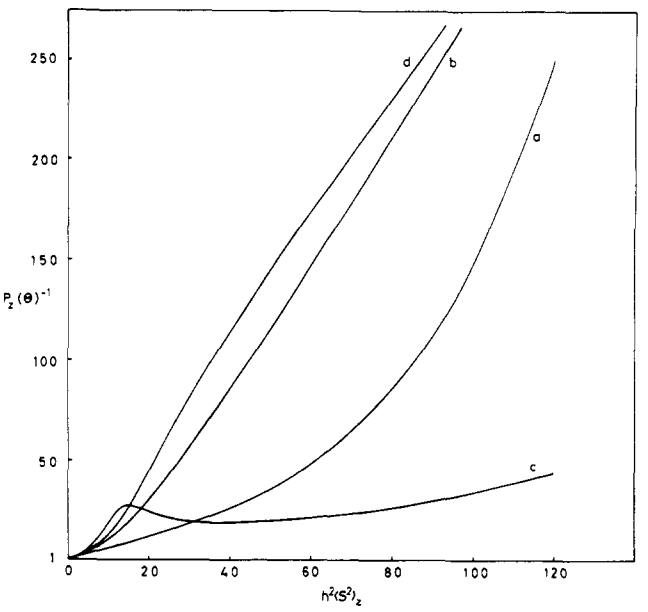

Figure 3. Scattering behavior of copolymer stars composed of a large center and 20 homodisperse branches. (a) Central unit and repeat units of the branches have the same refractive index increment; (b) refractive index increment of the center is zero, *i.e.*, the refractive index of the solvent equals that of the star center; (c) refractive index of the solvent is between the refractive indices of the two components; (d) scattering behavior of a corresponding star with point center.

crements on the particle scattering factor for a star with a large center ($M_c/M_s = 10^5$, $b_c/b_s = 50$, $DP_{ns} = 10^4$). In curve a both center and side chains have the same dn/dc. The scattering behavior is almost competely determined by the spherical center. Only at small angles are steeper increases of $P(\Theta)^{-1}$ found and these are due to the mean-square radius of gyration of the whole molecule being larger than that of the center. No detailed information can be gained from such scattering curves. In curve b the refractive index increment of the center is $\nu_c = 0$; it follows then from eq 28 for this star that $\nu_s = 1.5$. Light is not scattered by the center; the star resembles a "ghost star" where the side chains appear to be grafted onto the surface of an invisible sphere. Such a star should behave as if it had the same number of side chains but a point center. Comparison with curve d shows that this is indeed the case.

Very strange scattering behavior is obtained if the refractive index of the solvent lies between those of the two components, because then ν_c and ν_s differ in sign. Positive and negative terms now appear in the sum of eq 45 in I and of eq 19; the conflicting effects make an interpretation of the scattering curve very difficult. Curve c gives an example; it is tempting, but unsafe, to correlate the maximum with a characteristic length within the star molecule; clear information on the molecular structure can scarcely be gathered from such curves. Benoit and Froelich[9] discuss in their treatment of light scattering from block copolymers a case with an apparent negative mean-square radius of gyration. Such a case will also occur for these star molecules if as may be seen from eq 17.

$$g_s g_c(m_c M_s \alpha f N + m_s M_c)(G_{10} + \langle S^2\rangle_{0c} + \langle S^2\rangle_{0s}) > g_s^2 m_s M_s (G_{20} + 2\langle S^2\rangle_{0s}) + g_c^2 m_c M_c 2 \langle S^2\rangle_{0c} \quad (24)$$

Apparent Molecular Weight and Mean-Square Radius of Gyration. The apparent and true weight-average molecular weights are related by the simple equation

$$M_{w,app} = M_w + (M_w - M_n)(g_s^2 - 1) \quad (25)$$

where for homodisperse side chains

$$M_w - M_n = (1 - \alpha) N M_s m_s \quad (26a)$$

and for polydisperse side chains

$$M_w - M_n = \frac{\beta + (1 - \alpha)}{1 - \beta} M_s m_s \quad (26b)$$

Thus, for homodisperse star molecules the correct molecular weight is obtained in any case, while for stars with polydisperse side chains the additional term in eq 25 does not vanish even if $\alpha = 1$. This is in agreement with the well-known results of Bushuk and Benoit.[9,10] These authors express the relationship between $M_{w,app}$ and M_w quite generally by two heterogeneity parameters P and Q

$$M_{w,app} = M_w + 2P(g_s - g_c) + Q(g_s - g_c)^2 \quad (27)$$

where Q is a quantitative measure of the heterogeneity in composition, while P is related additionally to the molecular heterogeneity. For instance, one has $P = 0$ if the copolymer is homodisperse in mass, but $Q \neq 0$.

Equation 25 can also be brought into the general form of eq 27 with the heterogeneity parameters

$$P = (M_w - M_n) m_c \quad (28a)$$

and

$$Q = (M_w - M_n) m_c^2 = P m_c \quad (28b)$$

Equation 28b indicates that for stars the heterogeneity in composition is directly related to the heterogeneity in mass. Because of this direct proportionality only two measurements in solvents with different refractive indices are necessary for the stars, instead of the three solvents required in the general case of eq 27.

For practical reasons, it is advisable to select properly chosen classes of solvents. In the one class the solvent should have a rather low refractive index. Then ν_c and ν_s are comparatively high and the difference between M_w and $M_{w,app}$ is small and can often be neglected. In the other class the solvent should have a refractive index very close to that of the central unit so that ν_c becomes zero. If, in this

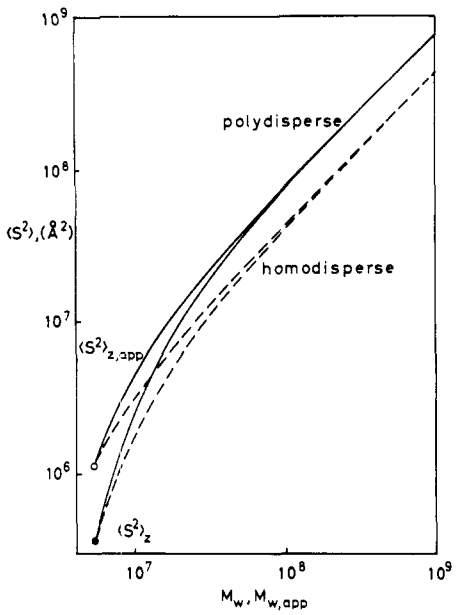

Figure 4. Apparent and true mean-square radii of gyration as a function of the apparent or true molecular weight of 20-star molecules. Solid lines correspond to branches with most-probable length distribution and broken lines represent homodisperse branches. The calculations are performed for $M_c/M_s = 10^5$ and $b_c/b_s = 50$.

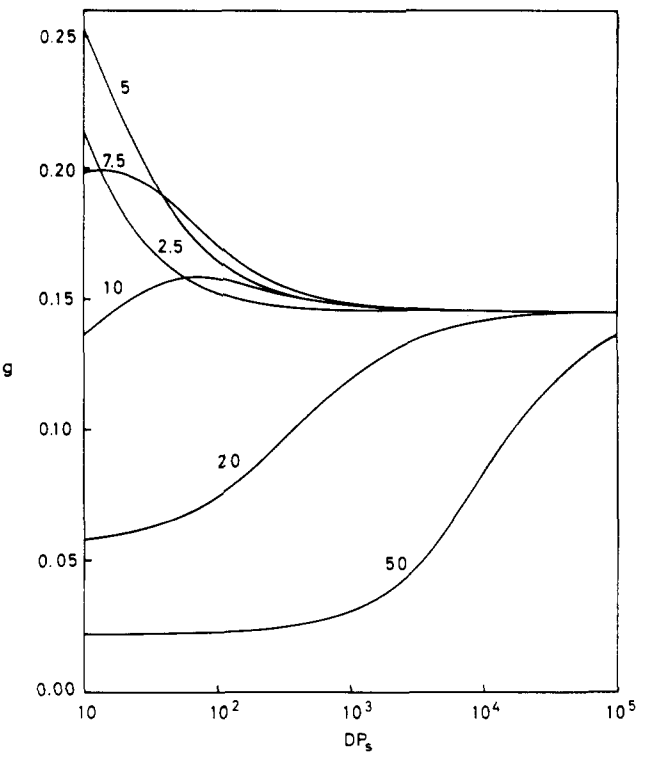

Figure 5. The g factor as a function of the side-chain length for stars with large centers. The figures indicate the ratio b_c/b_s; M_c is varied according to $M_c^{1/3} = \text{const} b_c$.

case, ν_s is used instead of the average index increment ν, the molecular weight and the mean-square radius of gyration of the grafted side chains are obtained (because m_s cancels out). Figure 4 shows the dependence of the mean-square radii of gyration on the molecular weight for the two cases. The dotted lines correspond to the homodisperse stars, while the full lines give the behavior of stars with polydisperse side chains. As expected, the mean-square radii of the polydisperse stars are larger than those of the homodisperse stars of the same molecular weight.

The larger apparent mean-square radii of gyration in solvents in which the star center is not visible appear surprising, but this behavior has a simple explanation. The two lines for the homodisperse and polydisperse stars end in a common point indicated by the open circle in Figure 4. This point represents the mean-square radius of gyration of 20 small repeat units of type s distributed at random on the surface of the invisible sphere of the center and resembles, in some respects, a hollow sphere. The full circle in Figure 5, however, represents the mean-square radius of gyration of the same 20 units distributed on the surface of a visible sphere. Since for a hollow sphere $\langle S^2\rangle = r^2$ [11] is larger than for a compact sphere, $\langle S^2\rangle = \frac{3}{5} r^2$ [12], of the same radius r, it is clear that there should be a similar difference for the two star models. This difference disappears for very long side chains because then the mass and the size of the center are negligible compared with the mass and size of the grafted side chains.

The g Factor. Branching in macromolecules is often efficiently described by the ratio of the mean-square radii of gyration of the branched and linear molecules at same values of the molecular weight

$$g = \langle S^2\rangle_{\text{branched}}/\langle S^2\rangle_{\text{linear}} \tag{29}$$

This ratio, as defined above, is sufficient for use with homodisperse star molecules with point centers, but the scope of its definition has to be enlarged to accommodate branched molecules with a certain molecular weight distribution. Zimm and Stockmayer[13] calculated mean values $\langle g\rangle$ by averaging g, defined by eq 29, with respect to the molecular weight distribution of the branched samples. This procedure necessarily implies comparison of the dimensions of the branched and linear products with identical molecular weight distributions. Application of the $\langle g\rangle$ values defined in this way to actual problems brings about serious difficulties, as in most cases linear and branched samples have vastly different molecular weight distributions.

The following definition appears reasonable for star molecules from both the theoretical and practical standpoint

$$g = \langle S^2\rangle_{z,\text{branched}}/\langle S^2\rangle_{z,\text{linear}} \tag{30}$$

where the linear chains have the length distribution of the branches in the star molecule; the two z-average values have to be taken at the same weight-average molecular weight. The g factor, so defined, can be calculated from eq 39 of I for polydisperse branches and from eq 17 for homodisperse branches, by use of

$$\langle S^2\rangle_{z,\text{linear}} = \frac{b_s^2}{4}\frac{M_{w,\text{star}}}{M_s} = \frac{b_s^2}{4(1-\beta)}[2 + (f-1)\alpha] \tag{31}$$

(polydisperse branches)

$$\langle S^2\rangle_{z,\text{linear}} = \frac{b_s^2}{6}\frac{M_{w,\text{star}}}{M_s} = \frac{b_s^2}{6}N[1 - (f-1)\alpha] \tag{32}$$

(homodisperse branches)

The g factor has been assumed in the past to be a unique function of the number of branches.[13-15] Figures 5 and 6 demonstrate, however, that in the more general case g depends also on the length of the branches and on α, the probability of grafting.

In the plot of Figure 5, the size of the spherical centers is assumed to increase with the molecular weight as

$$b_c = \text{const} M_c^{1/3} \tag{33}$$

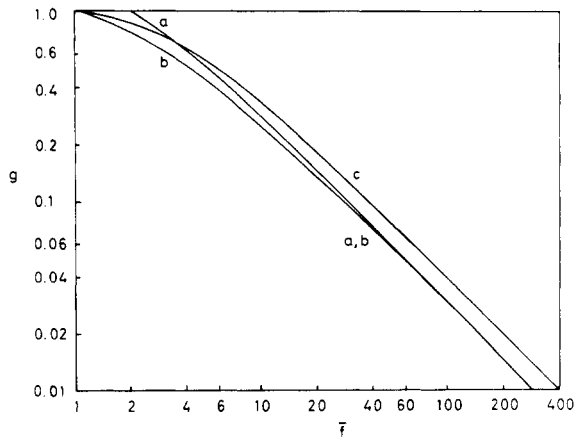

Figure 6. Limiting values of g as a function of the average number of branches for (a) stars with homodisperse branches ($\alpha = 0.1$); (b) regular homodisperse stars ($\alpha = 1$); (c) stars with polydisperse branches (most-probable length distribution) ($\alpha = 1$).

In the limit of large and small central units the curves of Figure 5 can be easily interpreted. Large compact spheres have small dimensions compared with those of linear chains of the same molecular weight. Hence, g starts at a very low value for short chains and gradually approaches a limiting value for very long chains. This limiting value is identical for all types of central units in the star, because at large chain lengths weight and dimensions of the central unit become negligible compared with those of the branches. For stars with small central units this limiting value of g is approached from larger values for short branches, because here the bond lengths of the central unit and the side chain units have approximately the same size, resulting in g factors close to 1 for very short side chains. The behavior of stars with moderately large centers is rather complicated and appears not accessible to interpretation in simple terms.

The limiting g values are given by

$$g \longrightarrow 4\frac{1 + (f - 1)\alpha}{[2 + (f - 1)\alpha]^2} \quad \text{(polydisperse branches)} \tag{34}$$

$$g \longrightarrow \frac{1 + 3(f - 1)\alpha}{[1 + (f - 1)\alpha]^2} \quad \text{(homodisperse branches)} \tag{35}$$

and these equations hold exactly for star molecules with point centers.[16]

It is of interest that for large numbers of branches g depends uniquely on the number average $\alpha f = \bar{f}$ of branches per molecule, while at small $\bar{f}$ it also depends on the probability α. See Figure 6.

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Polymer Normal Mode Analysis by Inelastic Light Scattering

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ABSTRACT: We have analyzed theoretically the autocorrelation function and spectrum of light inelastically scattered from a dilute solution of flexible polymer chains, each of which has a small but strongly scattering "label" conjugated to one or both ends or to the middle. Scattering from the polymer itself is nulled by refractive index matching. The label is postulated to be small enough that its influence on the hydrodynamic normal modes of the polymer is insignificant. Calculations indicate that intramolecular normal modes of the polymer chain, as they are manifested in the motion of the label, contribute strongly to the scattering spectrum at moderate chain lengths and scattering angles.

I. Introduction

In his fundamental paper of 1964,[1] and in several later ones,[2,3] Pecora raised the goal of using inelastic laser light scattering to detect intramolecular modes of motion in flexible polymer chains. This goal has been steadily pursued, notably by Frederick and coworkers,[4–6] but the pursuit has been difficult, because of the low scattering intensity contributed by the internal modes relative to translational diffusion and the stringent requirements for very high polymer molecular weight and monodispersity.

This paper presents a theoretical analysis of a new approach to this problem. We imagine that a dense, strongly scattering "label" is conjugated to the polymer chain at one or two points and that the solvent refractive index is chosen to match that of the polymer. Then scattering arises only from the label, which is supposed to have a substantial excess polarizability relative to the solvent. At the same time, the label is postulated to be small enough that its influence on the hydrodynamic normal modes of the polymer chain is insignificant. Our analysis of this model demonstrates that intramolecular normal modes of the polymer