Particle Scattering Factors of Some Branched Polymers

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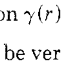
ABSTRACT: The particle scattering factors of (i) star molecules, (ii) f-functional random polycondensates and randomly cross-linked polymers, and (iii) nonrandomly branched polycondensates are compared. Branching is found to cause in Zimm plots an upturn of the angular distribution. Polydispersity reduces this upturn, and in randomly branched polymers the upturn is just balanced by the large polydispersity; these branched polymers are indistinguishable from linear chains which have the Schulz–Flory most probable molecular weight distribution. In Kratky plots where $h^2P(h)$ is plotted against h a maximum occurs at values of $u = h\langle S^2\rangle^{1/2}$ between 4.9 and 1.9 depending on the polydispersity and the number of branches per molecule. Star molecules with less than four rays exhibit no maximum. The maximum becomes more pronounced as the ray number is increased and it is shifted toward lower values of h. At very large ray number a limiting curve is obtained which for star molecules with polydisperse rays is identical with that of the nonrandom polycondensates of the AB_f type. It is also identical with the angular dependence derived by Pekeris and by Debye–Bueche on the basis of space correlation function $\gamma(r) = \exp(-r/a)$. The particle scattering factor of the nonrandom polycondensate of the  $A\!-\!\!<^{B}_{C}$ type is shown to be very similar to that of star molecules with polydisperse rays. The function can be expressed by the equation for the stars where, however, the chain number f is now the sum of outer and inner chains. The chain number can be determined from the asymptotic slope of the straight line in a $h^4P(h)$ plot. Application of this procedure is limited by the fact that for molecules with $\langle S^2\rangle_z < 200$ nm^2 the asymptote is influenced by the structure of a chain segment.

Investigation of molecular structures in solution by means of light scattering is now a common and widely used technique in polymer science. Interest was focused in the past mainly on the thermodynamic properties of solutions, on the molecular weight of the sample, and on its mean square radius of gyration.[1] It is well known, however, that much more information on the structure of the polymer can be extracted from the full curve of the particle scattering factor.[2] For experimental reasons full use cannot be made of this information in most cases. The dimensions of the molecules are often too small compared with the wavelength of the light; the root mean square radius $\langle S^2\rangle^{1/2}$ must exceed $\lambda/20$ to become detectable by scattering experiments, and a similar relationship holds for the dimensions of submolecular structures. These conditions require molecules of more than 100 nm in $\langle S^2\rangle^{1/2}$, and linear polymers of that size are not frequently observed.[40] This limitation does not apply to branched polymers. Stockmayer and Flory have shown,[3,4] now more than 30 years ago, that the weight average molecular weight M_w increases sharply near a critical extent of reaction or branching probability where gelation takes place. The molecular weight can reach in a macroscopic gelling system virtually infinitely large size. Thus, a careful consideration of the particle scattering factors from branched structures is promising as it will provide a much deeper insight in the structure than a mere determination of the relationship between $\langle S^2\rangle_z$ and M_w can give.

Equations for M_w, $\langle S^2\rangle_z$, and the particle scattering factors $P_z(h)$ for various branching models have been published,[5–18] and formulas for other models can be derived by means of the cascade theory[8–18] or more elementary techniques in simple cases.[5–7] These expressions are, however, often complicated and extensive computer work is needed in most cases before the experimental scattering curves can be interpreted by the formulas of the different models. The purpose of this paper is to emphasize some common and significant features of the particle scattering factors of branched molecules. Special plots are suggested which will make interpretation of scattering curves easier and more instructive than has been possible before. The features of the particle scattering factors described in this paper are probably quite general although strictly speaking all formulas given below apply to polymers in the theta state only.

Types of Branched Molecules

Linear chains are obtained by reaction of monomer units which have two functionalities. In order to get branching some of the monomers in the system must have at least three functionalities. Obviously, quite a large number of different branched structures are conceivable even if the fraction of the branching units in the polymer is kept constant. This fact renders the discussion to be confined to a selection of branched structures. The following three classes are considered in some detail: (i) star molecules; (ii) f-functional random polycondensates, random cross-linking; (iii) nonrandomly branched polycondensates.

The formulas derived for these classes of structures still encompass a large number of different models, too large to permit a comprehensive survey of the common and significant features of branched molecules here. Therefore, a first discussion is made with limiting structures where either the molecular weight is large such that the dimensions of star centers or branching points can be neglected or where the branching density has only a little influence on the particle scattering factors and the other conformational properties.

Limiting Branched Structures

It is a characteristic feature of the branched structures that their conformational properties are comprehensively described by their link probabilities (for instance by the link probability β for the formation of a chain and the link probability γ of the formation of a branching point). The link probabilities used in this paper are simply the extents of reaction of the various functional groups of a monomer. These link probabilities can in most cases be derived from known kinetic constants of the polymer formation.[13,15] In all cases the properties of linear chains are obtained by setting either the branching probability to zero or the functionality of the branching units to $f = 2$.

The particle scattering factors of linear chains are given mostly in terms of their mean square radii of gyration. Indeed, the link probability α of a linear chain can easily be eliminated by $\langle S^2\rangle_z$ if the degree of polymerization is large and if the bond length b is small compared with the wavelength of the light (See Appendix 1). The latter condition is certainly valid for any polymer if the wavelength of the visible light is used, but it does not hold for all angles in the case of small angle x

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* Dedicated to Maurice L. Huggins on his 80th birthday.

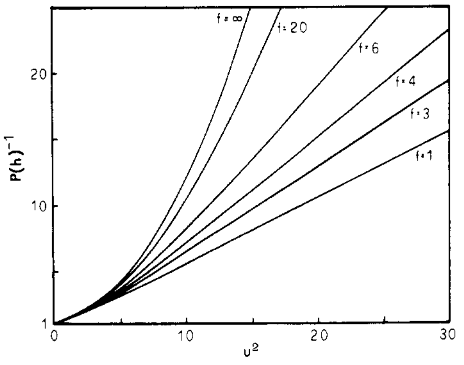

Figure 1. Plot of the reciprocal particle scattering factor $P(h)^{-1}$ of star molecules against $u^2 = \langle S^2\rangle h^2$. The numbers denote the ray numbers per molecule.

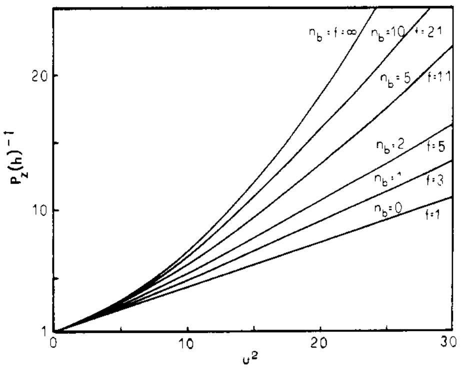

Figure 2. Plot of $P_z(h)^{-1}$ against $u^2 = \langle S^2\rangle_z h^2$ for star molecules with f polydisperse (most probable distribution) rays and for nonrandom polycondensates of the $\mathrm{A}{-}\!<^{\mathrm{B}}_{\mathrm{C}}$ type with n_{b} branching points per molecule, respectively. The case $f = 1$ corresponds to linear chains and randomly branched f-functional polycondensates.

ray and small-angle neutron scattering, where λ is in the range of 0.154 to 2 nm. In the light-scattering region, however, the approximate equations for $P_z(h)$ agree within less than 1% with the exact formulas if $P_{\mathrm{w}} > 100$.

Elimination of the link probabilities by $\langle S^2\rangle_z$ is not possible in all cases. Branched polymers are characterized quite often by a huge molecular polydispersity; in these cases a large weight average M_{w} does not ensure a large number average M_{n}. Nevertheless, for very large molecular weights, and if the branching density has exceeded a certain minimum value, the particle scattering factor becomes insensitive to the exact branching density up to rather high values of arguments of $h^2\langle S^2\rangle_z$ ($h = (4\pi/\lambda)\sin\theta/2$, where θ is the angle of scatter). See Figure 1. At that limit the link probabilities can be eliminated by either the molecular weight or the mean square radius of gyration. Tables I and II give the relationships for $P_z(h)$ and $\langle S^2\rangle_z$ for these limiting structures.

The Particle Scattering Factors of the Limiting Structures

Plot of $P_z(h)^{-1}$ as a Function of $h^2\langle S^2\rangle_z$. The effect of branching is demonstrated by Figures 1 and 2 where the reciprocal particle scattering factor $P_z(h)^{-1}$ is plotted against $u^2 = h^2\langle S^2\rangle_z$. In this plot all curves show the same initial slope of 1/3 corresponding to the power series expansion of $P_z(h)^{-1}$

$$P_z(h)^{-1} = 1 + \tfrac{1}{3}h^2\langle S^2\rangle_z - \ldots \qquad (1)$$

which holds generally for any type of particle.

With the exception of the f-functional randomly branched polycondensates all curves exhibit an upturn at larger values of u^2. This upturn becomes more pronounced as the number of rays in the star molecules is enlarged and it is stronger for regular stars with monodisperse rays than for the corresponding stars with a fairly broad length distribution of rays. This behavior indicates influence of a molecular polydispersity, which tends to reduce the upturn due to branching. A similar effect is observed with the nonrandom polycondensate of the $\mathrm{A}{-}\!<^{\mathrm{B}}_{\mathrm{C}}$ type, where again the upturn is increased with increasing branching density. For large molecular weight a limiting curve is obtained which corresponds to the particle scattering factor of the nonrandom polycondensates of the AB_f type. The nonrandom character of the $\mathrm{A}{-}\!<^{\mathrm{B}}_{\mathrm{C}}$ and AB_f polymers is expressed by the constraint that a group A can react with group B or C only (i.e., $\alpha = \beta + \gamma$) or

Table I
Particle Scattering Factors of Some Linear and Branched Molecules[a]

(1) Linear Chains

Monodisperse coils[36]

$$P(h) = (2/u^4)[\exp(-u^2) - (1 - u^2)] \qquad (1.1)$$

Polydisperse coils, most probable length distribution[37]

$$P_z(h) = (1 + u^2/3)^{-1} \qquad (1.2)$$

(2) Star Molecules with Rays which Follow Gaussian Statistics

Monodisperse rays[5,7a,10] (f = number of rays)

$$P(h) = \frac{2}{fV^2}\left[V - (1 - \exp(-V)) + \frac{f-1}{2}(1 - \exp(-V))^2\right] \qquad (2.1)$$

where

$$V = \frac{f}{3f-2}u^2 \qquad (2.1.1)$$

Polydisperse rays, most probable distribution[10]

$$P_z(h) = \frac{1 + u^2/3f}{(1 + u^2(f+1)/6f)^2} \qquad (2.2)$$

(3) Branched Polycondensates

Random f-functional polycondensates, A_f-type monomers[8]

$$P_z(h) = (1 + u^2/3)^{-1} \qquad (3.1)$$

Nonrandom $f + 1$-functional polycondensates, AB_f-type monomers (constraints: group A can react with B groups only) (Appendix 2)

$$P_z(h) = (1 + u^2/6)^{-2} \qquad (3.2)$$

Nonrandom polycondensates of the $\mathrm{A}{-}\!<^{\mathrm{B}}_{\mathrm{C}}$ type monomers[9] (constraints: group A can react with group B with probability β, or group A can react with group C with probability γ; all other reactions are excluded)

$$P_z(h) = \frac{1 + Cu^2/3}{[1 + (1 + C)u^2/6]^2} \qquad (3.3)$$

where

$$C = \left[(\beta + \gamma) + \frac{2\beta\gamma}{1 - \beta - \gamma}\right]^{-1}(\beta^2 + \gamma^2)$$

[a] The formulas are valid (i) for Gaussian end-to-end distribution of subchains which connect two chain elements of the polymer and (ii) for $b \ll \lambda$ where b is the effective bond length and λ the wavelength of the light; $h = (4\pi/\lambda)\sin\theta/2$, $u^2 = h^2\langle S^2\rangle_z$; θ is the angle of scatter and $\langle S^2\rangle_z$ is the mean square radius of gyration. The index z indicates the z average; $u^2 = h^2\langle S^2\rangle_z$.

Table II
Mean Square Radii of Gyration and Degrees of Polymerization for Some Linear and Branched Molecules ($P_w \gg 1$)[g]

Type of polymer	$\langle S^2\rangle_z/b^2$	P_w	P_n	$\langle S^2\rangle_z/b^2$	Ref
Monodisperse chains		P	P	$P/6$	1
Polydisperse chains[a]	$\alpha/[1-\alpha^2]$	$[1+\alpha]/[1-\alpha]$	$1/[1-\alpha]$	$P_w/4$	1, 8
Random A_f polycondensates[b]	$\dfrac{f\alpha}{2(1+\alpha)[1-\alpha(f-1)]}$	$\dfrac{1+\alpha}{1-\alpha(f-1)}$	$\dfrac{1}{1-\alpha(f/2)}$	$P_w\dfrac{f-1}{2f}$	8
Nonrandom AB_f polycondensates[c]	$\dfrac{\alpha}{1-\alpha}-\dfrac{\alpha^2/f}{1-\alpha^2/f}$	$\dfrac{1-\alpha^2/f}{(1-\alpha)^2}$	$\dfrac{1}{1-\alpha}$	${P_w}^{1/2}\left(\dfrac{f}{f-1}\right)^{1/2}$	Appendix 2
Nonrandom, $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ polycondensates[d]	$\dfrac{\beta+\gamma}{1-\beta-\gamma}-\dfrac{\beta^2+\gamma^2}{1-\beta^2-\gamma^2}$	$\dfrac{1-\beta^2-\gamma^2}{(1-\beta-\gamma)^2}$	$\dfrac{1}{1-\beta-\gamma}$	$\dfrac{{P_w}^{1/2}}{[2\gamma(1-\gamma)]^{1/2}}-\dfrac{1-2\gamma(1-\gamma)}{2\gamma(1-\gamma)}$	9
Monodisperse stars[e]	$\dfrac{3f-2}{6f}N$	fN	fN	$P_w\dfrac{3f-2}{6f^2}$	6, 7, 10
Polydisperse stars[f]	$\dfrac{(1+\beta)+2(f-1)}{2(f+\beta)(1-\beta)}$	$\dfrac{f+\beta}{1-\beta}$	$\dfrac{f}{1-\beta}$	$P_w\dfrac{f}{(f+1)^2}$	7, 10

[a] α probability of reaction of a functional group. [b] α probability of reaction of one of the f A groups. [c] α probability of reaction of an A group with one of the f B groups. [d] β probability of reaction of a B group with an A group (probability of chain propagation). γ probability of reaction of a C group with an A group (branching probability). [e] N degree of polymerization of a ray. f number of rays per star molecule. [f] β probability of reaction of a functional group from a ray. f number of rays per star molecule. [g] b = effective bond length; P_w, P_n = weight and number average degrees of polymerization, respectively.

with the corresponding f B groups (i.e., $\alpha = f\beta$), respectively; all other reactions are excluded. In contrast all cross reactions are allowed in random condensation.

No curvature is obtained for the random polycondensates. Moreover, the particle scattering factors of the branched polycondensates are indistinguishable from that of linear chains obeying the Schulz–Flory most probable molecular weight distribution. This behavior is typical for all randomly branched polymers and it is caused by the large polydispersity which in these cases just balances the effect of branching.[8,11-13,19,20] This problem of polydispersity will be discussed below in greater detail.

Behavior at Medium Values of u^2 (Kratky plot). The effect of branching is displayed even more marked in a plot of $u^2P_z(h)$ which in small-angle x-ray scattering (SAXS) or in small-angle neutron scattering (SANS) is frequently used for interpretation of linear chains (Kratky plot). The Kratky plots of the corresponding curves in Figures 1 and 2 are shown in Figures 3 and 4. Linear Gaussian chains are known to reach asymptotically plateau values of 2 and 3 for monodisperse and polydisperse chains (most probable distribution), respectively. The same behavior is obtained for the unfractionated randomly branched polycondensates.

The most striking feature of the particle scattering factors of the other branched models is the appearance of a maximum. This maximum becomes more pronounced as the number of rays of the star molecules is increased. Its position occurs at a fairly large u value for the 4-stars and is shifted to lower u values with increasing ray number. Simultaneously, the maximum value is lowered. Both types of stars show the behavior; the drift of the maximum position is, however, smaller for the monodisperse than for the polydisperse stars. The position and value of the maximum reaches limits for very

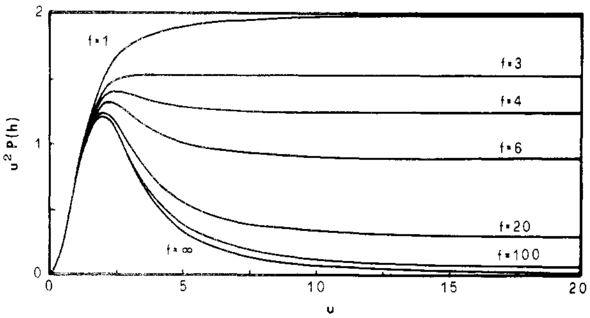

Figure 3. Kratky plot of $P(h)$ for homodisperse star molecules. Meaning of symbols as in Figure 1.

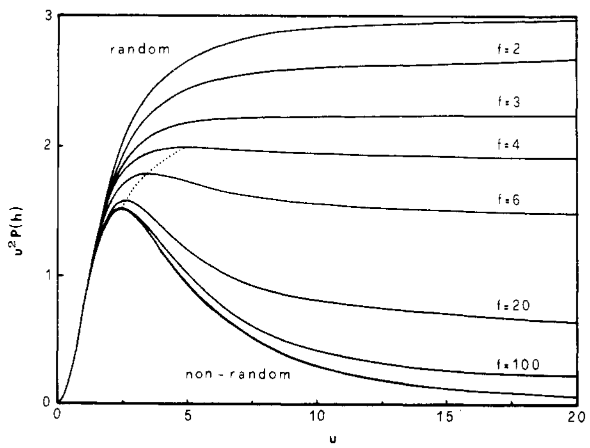

Figure 4. Kratky plot of $P_z(h)$ for stars with polydisperse rays (most probable distribution). The same behavior is obtained for the nonrandom $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ polycondensates where $f = n_b + f_B$ with f_B the number of B chains (see also Figure 6). Curve "nonrandom" corresponds to the AB_f-type polycondensates and curve "random" corresponds to the random f-functional polycondensates of the A_f type. The dotted line gives the position of maxima.

Table III
Maximum Position $u_{\max} = C_f{}^{1/2}$, Value of the Maximum $(u^2P_z(h))_{\max}$, and Values for the Asymptotic Plateau $(u^2P_z(h))_\infty$ for Star Molecules

	Monodisperse			Polydisperse		
f	$u_{\max}$	$(u^2P_z(h))_{\max}$	$(u^2P_z(h))_\infty$	$u_{\max}$	$(u^2P_z(h))_{\max}$	$(u^2P_z(h))_\infty$
2			2.00			2.66
3			1.55			2.25
4	2.522	1.422	1.25	4.899	2.000	1.920
5	2.313	1.349	1.04	3.873	1.875	1.660
6	2.194	1.324	0.889	3.464	1.800	1.469
8	2.117	1.294	0.688	3.098	1.714	1.185
10	2.083	1.279	0.566	2.928	1.667	0.992
20	1.997	1.250	0.290	2.657	1.579	0.542
50	1.964	1.238	0.118	2.526	1.531	0.231
100	1.952	1.227	0.0596	2.487	1.515	0.118
∞	1.940	1.217	0.0	2.449	1.500	0.0

large ray numbers. In general, the position and value of the maximum in the Kratky plot for polydisperse stars are given by the following two equations

$$u_{\max}{}^2 = 6f/(f-3) \tag{2}$$

$$u^2P_z(h)_{\max} = 1.5f/(f-1) \tag{3}$$

where f is the functionality of the star center unit. For monodisperse regular stars the position of the maximum has to be calculated from the implicit equation

$$V = \frac{1-\exp(-V)-(f-1)/2(1-\exp(-V))^2}{[1-(f-1)\exp(-V)]\exp(-V)} \tag{4}$$

where

$$V = \frac{3f-2}{2}u_{\max}{}^2 \tag{5}$$

Table III gives a list of $u_{\max}$ and $u^2P(h)_{\max}$ as a function of ray number f for both types of stars.

It is of interest that the maximum position of the nonrandom polycondensates of the type $\mathrm{A}{-}\!\!<^{\mathrm{B}}_{\mathrm{C}}$ and AB_f occurs exactly at the same value of $6^{1/2}$ as is obtained for polydisperse stars with large ray numbers. This fact has some practical relevance and will be discussed below.

Asymptotic behavior, $u^2 > 100$. Up to values of $u^2 = 10$ the particle scattering factors of polydisperse star molecules with more than ten rays can scarcely be distinguished from the scattering behavior of the nonrandom AB_f polycondensates. Both types of branched structures can be well represented by the particle scattering factor

$$P_z(h) = (1 + u^2/6)^{-2} \tag{6}$$

Differentiation between the two classes of branched structures becomes possible by consideration of the asymptotic behavior in the range of $u^2 > 100$. This asymptotic behavior is most instructively displayed in a plot of $u^4P_z(h)$. One readily verifies that this function reaches a constant plateau of 36 for the nonrandom AB_f polycondensates

$$u^4P_z(h) = \frac{u^4}{(1+u^2/6)^2} \xrightarrow[u^2]{\text{large}} 36 \tag{7}$$

while for star molecules with polydisperse rays one has

$$u^4P_z(h) = \frac{u^4(1+u^2/3f)}{[1+u^2(f+1)/6f]^2} \tag{8}$$

This function can in the range of $60 \le u^2 \le 250$ be well represented by the approximation

$$u^4P_z(h)_{\text{asympt}} = \left(\frac{6f}{f+1}\right)^2\left(\frac{0.83f-3}{f+1}\right)\left(1+\frac{u^2}{2.4f-6.3}\right) \tag{9}$$

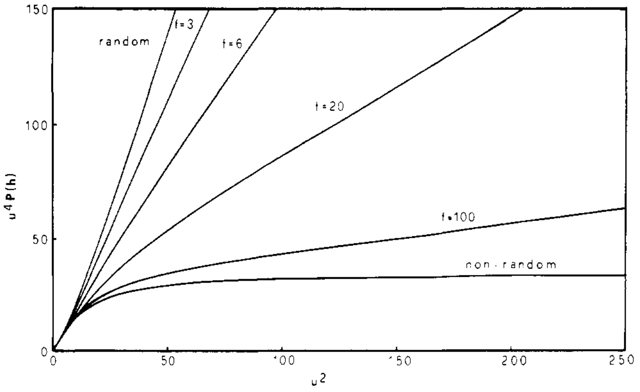

Figure 5. Plot of $u^4P_z(h)$ against u^2 for the particle scattering factors given in Figure 4.

which forms a straight line when the left side is plotted against u^2. Deviations of eq 9 from the exact relationship (eq 8) are less than 5% if $f < 250$. Figure 5 gives an example of this plot.

Similarly, for monodisperse regular stars one has

$$u^4P_z(h)_{\text{asympt}} = \frac{(3f-2)(f-3)}{f^2}\left(1+\frac{2f}{(3f-2)(f-3)}u^2\right) \tag{10}$$

which again is a straight line when plotted against u^2. The slope of this $u^4P_z(h)$ plot thus allows a rather simple determination of the number of rays per star molecule.

Behavior of the $\mathrm{A}{-}\!\!<^{\mathrm{B}}_{\mathrm{C}}$ Nonrandom Polycondensates.

Comparison of the scattering curves from the $\mathrm{A}{-}\!\!<^{\mathrm{B}}_{\mathrm{C}}$ type nonrandom polycondensates with those from the polydisperse star molecules reveals a striking similarity. This similarity suggests the impression that the scattering behavior of the $\mathrm{A}{-}\!\!<^{\mathrm{B}}_{\mathrm{C}}$ polymers is predominantly determined by the number of branches and not so much by the actual internal structure. Following this idea one first has to determine which kind of branches most influence $P_z(h)$. As illustrated in Figure 6, one can define B chains with number f_{B} equal to the number of free B end groups. On the basis of the number average degree of polymerization this number is $f_{\mathrm{B}} = (1-\beta)/(1-\beta-\gamma)$, where γ is the branching probability and $(1-\beta)^{-1}$ is the number average chain length of B chains.

Furthermore, one can define internal chains which are terminated at both ends by branching points, and finally one can define outer chains which are only bound to a branching

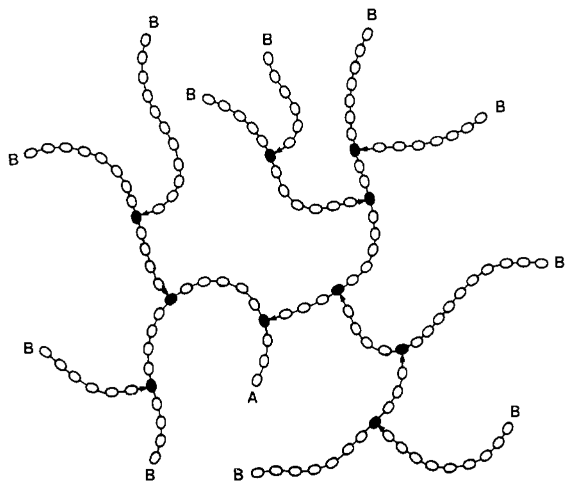

Figure 6. Structure of the nonrandomly branched polycondensates of the $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ type. Branching occurs at a C group and is indicated by an arrow. A chain leading from its branching point to a free B end group is called a B chain. The molecule has only one free A end group but $n_b + 1$ free B end groups where n_b is the number of branching units.

point at one end. The number of outer chains is simply $f_o = f_B + 1$, and the number of internal chains is $f_i = n_b - 1$ where n_b is the number of branching points. Since the number of branching points is the branching probability times the DP$_n$ one has $n_b = \gamma/(1 - \beta - \gamma)$. The total number of branches is the sum of outer and inner chains, thus

$$f = f_o + f_i = n_b + f_B = \frac{2\gamma}{1 - \beta - \gamma} + 1 \qquad (11)$$

The various structural parameters and their relations to the link probabilities are listed in Table IV.

The coefficient C in the particle scattering factor of eq 3.3 (Table I) is

$$1/C = \left[(\beta + \gamma) + \frac{2\beta\gamma}{1 - \beta - \gamma} \right] \Big/ (\beta^2 + \gamma^2) \qquad (12)$$

For large degrees of polymerization one has $(\beta + \gamma) \simeq 1$ and the coefficient takes the limiting form

$$1/C \rightarrow \left[1 + \frac{2\gamma(1 - \gamma)}{1 - \beta - \gamma} \right] \Big/ [1 - 2\gamma(1 - \gamma)] = \frac{f - (f - 1)\gamma}{1 - 2\gamma(1 - \gamma)} \qquad (13)$$

where use of eq 11 has been made. Hence, for large DP$_n$ the particle scattering factor may be written

$$P_z(h) = \left(1 + \frac{1 - 2(1 - \gamma)\gamma}{3[f - (f - 1)\gamma]} u^2\right) \Big/ \left(1 + \frac{(f + 1) - (f + 1 - 2\gamma)\gamma}{6[f - (f - 1)\gamma]} u^2\right)^2 \xrightarrow{\gamma \ll 1} (1 + u^2/3f)/(1 + (f + 1)/(6f)u^2)^2 \qquad (14)$$

As long as the branching probability γ is small, the particle scattering factor is similar to that of star molecules with polydisperse rays. Even for the highest branching probability $\gamma \simeq 0.5$ the error in the estimate of the number of branches is not larger than two when the formula for polydisperse stars is used. One has to keep in mind, however, that the meaning of f is different in the two models. While in star molecules the ray number is simultaneously the number of outer chains, the branch number f in the $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ polycondensate is the sum of outer and inner chains.

Table IV
Relationships between the Link Probabilities β and γ and the Structural Parameters of the Branched $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ Polycondensate Type (see Figure 6)

Wt av degree of polymerization	$P_w = (1 - \beta^2 - \gamma^2)/(1 - \beta - \gamma)^2$
No. av degree of polymerization	$P_n = (1 - \beta - \gamma)^{-1}$
Chain length of B chains	$P_{nB} = (1 - \beta)^{-1}$
No. of B chains per molecule	$f_B = (1 - \beta)/(1 - \beta - \gamma)$
No. of branches per B chain	$n_{bB} = \gamma/(1 - \beta)$
No. of branching points per molecule	$n_b = \gamma/(1 - \beta - \gamma)$
No. of outer chains	$f_o = f_B + 1$
No. of inner chains	$f_i = n_b - 1$
Total no. of chains per molecule	$f = f_o + f_i = 1 + 2\gamma/(1 - \beta - \gamma)$

At this point the question arises whether the nonrandom polycondensate can ever be distinguished from the scattering behavior of star molecules. In fact measurements of the angular dependence from one sample only will not give enough information. However, while f remains constant in a star molecule if the molecular weight is changed, it varies approximately in the same way as the molecular weight does for the $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ polymer.

Discussion

Origin of the Upturn of $P_z(h)^{-1}$. The upturn of the reciprocal particle scattering factor in a plot against h^2 appears as a typical sign for branching. The randomly branched f-functional polycondensates seem to be the only exception. The linear angular dependence in Zimm plots is identical with that of linear chains which obey the most probable length distribution, and this behavior has indeed been observed with these polymers.[13,19,20] When this property was stated theoretically,[8] the authors discussed this effect as a result of the broad molecular weight distribution of the randomly branched polycondensates. This interpretation was confirmed by Kajiwara[18] who succeeded in the calculation of particle scattering factors of monodisperse fractions from the f-functional polycondensates. He found again the characteristic upturn.

The particle scattering factor of cross-linked chains which obey the most probable molecular weight distribution also show rectlinear behavior in a Zimm plot.[11,12,19] Randomly cross-linked chains of uniform length or of less polydispersity reveal again the characteristic upturn which, however, is not strongly shaped.[12] Finally the upturn of the reciprocal particle scattering factor of stars with polydisperse rays is flatter than that for regular monodisperse stars. These findings justify the statement that branching causes an upturn of the reciprocal particle scattering factors when plotted against h^2, but this upturn is partly smoothed by a molecular polydispersity and can be fully compensated in some cases by the downturn due to the polydispersity. The latter is observed with randomly branched polycondensates or randomly cross-linked chains which show the most probable length distribution.

Determination of $\langle S^2 \rangle_z$ from the Position of the $h^2P_z(h)$ Maximum. The upturn observable in Zimm plots corresponds to the appearance of a maximum in plots of $h^2P_z(h)$.[12] As already mentioned the position of this maximum approaches quickly a constant value in the $u^2 = \langle S^2 \rangle_z h^2$ scale if the number of branches per molecule becomes larger than $f = 10$. This fact allows an estimate of $\langle S^2 \rangle_z$ from the position of the maximum in the h^2 scale.

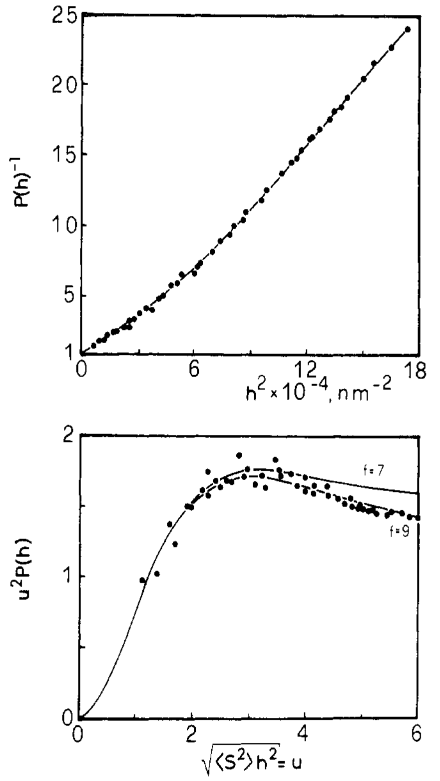

Figure 7. (a) Angular dependence of scattered light from a poly(divinylbenzene–styrene) star molecule in toluene; prepared by anionic technique. $M_{\mathrm{w,star}} = 16.7 \times 10^6$, $\langle S^2\rangle_{z,\mathrm{star}} = 1.98 \times 10^4$ nm^2; $M_{\mathrm{w,nucleus}} = 0.3 \times 10^6$, $\langle S^2\rangle_{z,\mathrm{nucleus}} = 3 \times 10^2$ nm^2. (b) Kratky plot of (a). The solid lines are theoretical curves for stars with $f = 7$ and $f = 9$ polydisperse rays.

$$\langle S^2\rangle_z = C_f/h_{\mathrm{max}}^2 \qquad (15)$$

where the values of $C_f = u_{\mathrm{max}}^2$ are given in Table III. In particular for large chain numbers one has $C_\infty = 6$ for stars with polydisperse rays and the AB$_f$ polymers and $C_\infty = 3.76$ for regular stars with monodisperse rays.

Using C_∞ the mean square radius of gyration would be determined about 50% smaller for a molecule with $f = 6$ than the molecule has in reality; for $f = 10$ the error is about 30% and for $f = 50$ it is only 6%. This possibility of an estimation of $\langle S^2\rangle_z$ by eq 15 is of great value. Samples which show a maximum have large $\langle S^2\rangle_z$, making determination of $\langle S^2\rangle_z$ from the initial slope of a Zimm plot very uncertain or even impossible since the initial curvature at very low angles may not be accessible to measurement with ordinary light-scattering instruments. The accuracy of the determination of $\langle S^2\rangle_z$ is increased by using the correct C_f value. To this end the number of branches must be known.

Determination of the Number of Branches from a Plot of $u^4P_z(h)$. The number of branches can be obtained either by a direct fit with eq 21 or 22 or from the slope to intercept ratio of the extrapolated straight line in a plot of $u^4i(h)$ against u^2, where $i(h)$ is the scattering intensity in arbitrary units. In order to find $u^2 = \langle S^2\rangle_z h^2$ the value of $\langle S^2\rangle_{z\infty}$ determined from eq 15 with C_∞ can be used as a first approximation. The chain number f obtained with this value from the $u^4i(h)$ plot can then be used for an improved $\langle S^2\rangle_z$ determination where now the value C_f, listed in Table III, has to be taken. With this refined value of $\langle S^2\rangle_z$ the chain number f can be obtained from the $u^4i(h)$ plot with good accuracy.

This procedure does not work, however, in all cases. For instance, a branched molecule with a mean square radius of gyration of $\langle S^2\rangle_z = 200$ nm^2 would have its asymptote ($60 \leq u^2 \leq 250$) at values of $0.3 \leq h^2 \leq 1.25$ nm^{-2}. This h^2 region corresponds to distances between two scattering points i and j of $0.9 \leq r_{ij} \leq 1.8$ nm, and average distances of this length are not governed by Gaussian statistics, which is the basis of the $P_z(h)$ calculations. Distances on a chain of that short length are determined by short-range interactions.[21] In other words, the asymptotic behavior will in these cases be significantly influenced by the actual structure of a statistical segment.

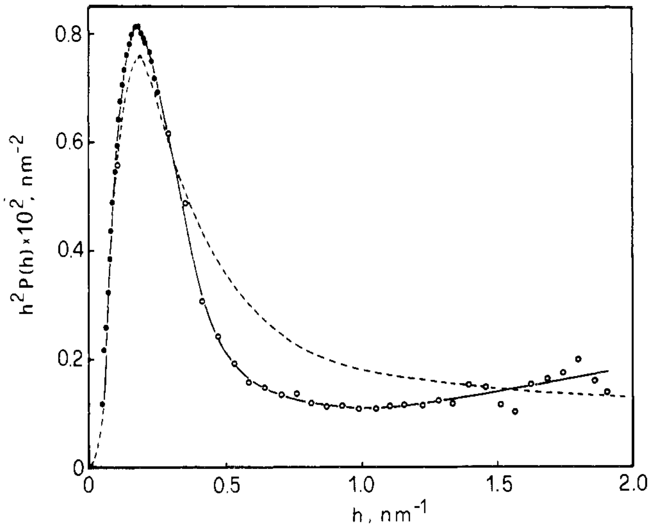

Figure 8. Kratky plot from small-angle neutron scattering of glycogen in D$_2$O. $M_{\mathrm{w}} = 1.59 \times 10^6$, $\langle S^2\rangle_z = 205$ nm^2. The dotted line gives the theoretical scattering behavior of a nonrandom $\mathrm{A}{-}{<}^{\mathrm{B}}_{\mathrm{C}}$ polycondensate, where $\gamma = 0.1$ (10% branching) was chosen.

Figure 7 gives an example of data for which this segmental structure evidently plays a role. The branched polysaccharide glycogen whose particle scattering factor has been measured by means of elastic small-angle neutron scattering[22] has a mean-square radius of gyration of $\langle S^2\rangle_z = 205$ nm^2 and a moleculr weight of $M_{\mathrm{w}} = 1.59 \times 10^6$. It shows a pronounced maximum at the point predicted with eq 3.2 or 3.3 when $\gamma = 0.1$ (corresponding to the average degree of branching of 10%) is used. There is no full agreement between the experiment and the theory of a homogeneously branched glycogen.[9] The deviations are caused by some heterogeneity in branching[23,24] and will be discussed in detail in a separate paper. Attention may be given, however, to the asymptote which in theory should show a continuous decrease, but which actually shows an increase. The increase of the function $h^2P_z(h)$ at large h values is typical of the scattering behavior from stiff segments.[12,25-27]

Figure 8 shows as another example the light-scattering behavior of a star molecule prepared by anionic technique.[28] These star molecules have a polydisperse divinyl benzene nucleus and several polystyrene rays. The scattering curves can be described by the model of stars with about seven to nine polydisperse rays per nucleus on the average. This ray number is appreciately smaller than the number 22 which is obtained from the molecular weights of the star, the nucleus, and the ray length.[29] This discrepancy is probably caused by the unavoidable fluctuation in the ray number which again will result in a levelling of the upturn in a Zimm plot or of the maximum height in a Kratky plot.

Other examples for the upturn for the nonrandom type polymers with the indicated maximum in the Kratky plot have been observed by light scattering with highly diluted solutions of intermediate structures of fibrin[30] and in concentrated solutions with aggregates of cellulose acetate in benzyl alcohol.[31] Neutron scattering from aggregates of polyethylene immersed in a matrix of deuterated polyethylene also exhibits the characteristic maximum in the Kratky plot.[32]

Interpretation by Means of Correlation Functions. The scattering patterns of the concentrated solutions of cellulose acetate have been interpreted by Berry et al.[31] with a space correlation function of the kind

$$\gamma(r) = \exp(-r/a) = \frac{\langle \eta(r_i)\eta(r_j)\rangle}{\langle \eta^2 \rangle} \qquad (16)$$

$$r = |r_i - r_j|$$

where η_i and η_j are the fluctuations of polarizability at positions r_i and r_j in space and $\langle \eta^2 \rangle$ is the mean square fluctuation which, of course, is independent of the position in space.

In fact, it is striking that application of eq 16 leads to a particle scattering factor[33,34]

$$P(h) = (1 + h^2a^2)^{-2} \qquad (17)$$

which is formally identical with eq 3.2 in Table I for the nonrandom polycondensates if the correlation length a is related to the mean square radius of gyration of the particle as

$$a^2 = \langle S^2 \rangle_z/6 \qquad (18)$$

The concept of correlation functions was introduced by Pekeris[33] and by Debye and Bueche[34] to describe inhomogeneities in solid material. The correlation length a is defined as that distance where the correlation of the fluctuations of scattering at $r = 0$ and $r = a$ is fallen to a value of e^{-1}. In dilute solutions the motion of molecules or particles can be assumed to be completely independent, and under these circumstances the correlation function $\gamma(r)4\pi r^2\,\mathrm{d}r$ is nothing else than the probability of finding another segment of the same molecule in the spheric shell of r and $r + \mathrm{d}r$, if the reference segment is at position $r = 0$;[35] outside of the domain of the molecule $\gamma(r)$ is zero. Hence, in such cases the correlation length is solely dependent on the mean square radius of gyration of the isolated molecule. One has to keep in mind, however, that $\gamma(r)$ is the length distribution in a particle *averaged* over all sizes of particles.[33] Particles of the same size and structure but different size distribution will have, therefore, different correlation functions. This is clearly seen by comparison of $\gamma(r)4\pi r^2\,\mathrm{d}r$ of the random and nonrandom trifunctional polycondensates. These correlation functions can be obtained by application of the Fourier theorem to the particle scattering factors.[34]

$$r\gamma(r) = \frac{1}{(2\pi)^3} \int_0^\infty P(h)h \sin(hr)\,\mathrm{d}h \qquad (19)$$

For the random polycondensates one finds

$$\gamma(r)4\pi r^2\,\mathrm{d}r = \frac{3}{4\pi}\frac{r}{\langle S^2 \rangle_z} \exp[-r(3/\langle S^2 \rangle_z)^{1/2}]\,\mathrm{d}r \qquad (20)$$

while for the nonrandom polymer the correlation function is

$$\gamma(r)4\pi r^2\,\mathrm{d}r = \frac{1}{8\pi}\left(\frac{6}{\langle S^2 \rangle_z}\right)^{3/2} r^2 \times \exp[-r(6/\langle S^2 \rangle_z)^{1/2}]\,\mathrm{d}r \qquad (21)$$

These polymers differ not so much in their branched structures as in their size distribution.[9]

Interpretation of $\gamma(r)$ for concentrated solutions is not simple, because now some order between different particles in solution will persist. The fluctuations between different particles will be correlated and will give rise to interparticle scattering. Therefore, the apparent mean square radius of gyration due to eq 18 will be larger than that of the isolated molecule. Defined aggregates in turn will behave like branched molecules, and $\langle S^2 \rangle_z$ will be that of the aggregate.

Summarizing this consideration one can state that the concept of correlation functions leads for isolated particles to the same scattering behavior as direct application of Debye's scattering equation when averaged over all sizes

$$P_z(h) = M_{\mathrm{w}}^{-1} \sum_x M_x w(x) \left(\frac{1}{x^2}\sum_i^x \sum_j^x \left\langle \frac{\sin(hr_{ij})}{hr_{ij}} \right\rangle\right) \qquad (22)$$

In this equation M_x is the molecular weight of a particle of the degree of polymerization x, $w(x)$ is the weight distribution of x, r_{ij} is the distance between scattering elements i and j, and the brackets $\langle\,\rangle$ indicate the average over all conformations.

In concentrated solutions and in solids the correlation function comprises the effect of particle and interparticle scattering. The correlation length a can only in rare and special cases be related to a mean square radius of gyration which has a simple meaning with respect to the actual structure of the particles.

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Appendix 1

Derivation of Equations for the Particle Scattering Factors at Large Degrees of Polymerization. (a) Random *f*-Functional Polycondensates. The particle scattering factor is given by Kajiwara et al.[8]

$$P_z(h) = \frac{1 - \alpha(f-1)}{1 + \alpha}\,\frac{1 + \alpha\exp(-h^2b^2/6)}{1 - \alpha(f-1)\exp(-h^2b^2/6)} \qquad (\mathrm{A1.1})$$

(For the definition of α see Table II footnote). In most cases of interest one has $b^2h^2 = b^2(4\pi/\lambda)^2 \sin^2\theta/2 \ll 1$, where λ is the wavelength of the scattering source (visible light, x rays, neutrons) and θ is the angle of scatter. Under these conditions the exponentials in (A1.1) can be expanded to yield

$$P_z(h) = \frac{1 - \alpha(f-1)}{1 + \alpha}\,\frac{1 + \alpha - \alpha b^2h^2/6}{1 - \alpha(f-1) + \alpha(f-1)b^2h^2/6}$$

$$P_z(h) = \frac{1 - \dfrac{\alpha}{1+\alpha}b^2h^2/6}{1 + \dfrac{\alpha(f-1)}{1-\alpha(f-1)}b^2h^2/6} \qquad (\mathrm{A1.2})$$

In branched polymers $\alpha(f-1) \simeq 1$ and $\alpha/(1-\alpha)b^2h^2/6 \ll 1$. Therefore,

$$P_z(h)^{-1} \simeq 1 + \left(\frac{\alpha(f-1)}{1-\alpha(f-1)} + \frac{\alpha}{1+\alpha}\right)b^2h^2/6 \qquad (\mathrm{A1.3})$$

and since[8]

$$\langle S^2 \rangle_z = \tfrac{1}{2}\left(\frac{\alpha(f-1)}{1-\alpha(f-1)} + \frac{\alpha}{1+\alpha}\right)b^2$$

one has

$$P_z(h) = (1 + \langle S^2 \rangle_z h^2/3)^{-1} \qquad (\mathrm{A1.4})$$

(b) Nonrandom $\mathrm{A}\!-\!\!<^{\mathrm{B}}_{\mathrm{C}}$ Type Polycondensates. Similarly, by expansion of the exponential in[9]

$$P_z(h) = \frac{(1-\beta-\gamma)^2}{1-\beta^2-\gamma^2}\,\frac{1 - (\beta^2+\gamma^2)\exp(-b^2h^2/3)}{[1 - (\beta+\gamma)\exp(-b^2h^2/6)]^2} \qquad (\mathrm{A1.5})$$

one finds

$$P_z(h) = \frac{1 + \dfrac{\beta^2+\gamma^2}{1-\beta^2-\gamma^2}b^2h^2/3}{\left[1 + \dfrac{\beta+\gamma}{1-\beta-\gamma}b^2h^2/6\right]^2} \qquad (\mathrm{A1.6})$$

This can be written as

$$P_z(h) = \frac{1 + C\langle S^2 \rangle_z h^2/3}{[1 + (1+C)\langle S^2 \rangle_z h^2/6]^2} \qquad (\mathrm{A1.7})$$

where

$$\langle S^2\rangle_z = \left(\frac{\beta+\gamma}{1-\beta-\gamma} - \frac{\beta^2+\gamma^2}{1-\beta^2-\gamma^2}\right)b^2$$

and

$$C = (\beta^2+\gamma^2)\left[(\beta+\gamma) + \frac{2\beta\gamma}{1-\beta-\gamma}\right]^{-1} \qquad \text{(A1.8)}$$

The link probabilities β and γ are defined in Table II footnotes.

(c) Star Molecules with Polydisperse Rays. Neglecting the mass fraction of the f-functional star centers the particle scattering factor is[10]

$$P_z(h) = \frac{1-\beta}{f+\beta}\left[\frac{1+\beta\exp(-b^2h^2/6)}{1-\beta\exp(-b^2h^2/6)} + \frac{(1-\beta)(f-1)\exp(-b^2h^2/3)}{[1-\beta\exp(-b^2h^2/6)]^2}\right] \qquad \text{(A1.9)}$$

Expansion of the exponentials yields

$$P_z(h) = \frac{1-\beta}{f+\beta} \times \left[\frac{(1-\beta)[1+\beta+(f-1)] + [\beta^2-(1-\beta)(f-1)]b^2h^2/3}{(1-\beta+\beta b^2h^2/6)^2}\right]$$

and after some rearrangements

$$P_z(h) = \frac{1 + \dfrac{\beta^2-(1-\beta)(f-1)}{(f+\beta)(1-\beta)}b^2h^2/3}{(1+[\beta/(1-\beta)]b^2h^2/6)^2} \qquad \text{(A1.10)}$$

For large ray length $\beta \simeq 1$ and[10]

$$\langle S^2\rangle_z = \frac{1+\beta+2(f-1)}{2(f+\beta)(1-\beta)} \simeq \frac{f}{(f+1)(1-\beta)} \qquad \text{(A1.11)}$$

$$\frac{\beta}{1-\beta} \simeq \frac{f+1}{f}\langle S^2\rangle_z \qquad \text{(A1.12)}$$

$$\frac{\beta^2-(1-\beta)(f-1)}{(f+\beta)(1-\beta)} \simeq \frac{1}{(f+1)(1-\beta)} = \langle S^2\rangle_z/f \qquad \text{(A1.13)}$$

Thus

$$P_z(h) = \frac{1+\langle S^2\rangle_z h^2/(3f)}{[1+\langle S^2\rangle_z h^2(f+1)/(6f)]^2} \qquad \text{(A1.14)}$$

(d) Monodisperse Stars.[5,7a,10] The particle scattering factor is[10]

$$P(h) = \left(P_2 + \frac{f-1}{N}P_1{}^2 + \frac{P_1}{N}\right)\Big/(fN) \qquad \text{(A1.15)}$$

where

$$P_1 = \frac{1-\exp(-hb^2N/6)}{1-\exp(-h^2b^2/6)}\exp(-h^2b^2/6) \qquad \text{(A1.16)}$$

$$P_2 = 1 + \frac{2\exp(-h^2b^2/6)}{1-\exp(-h^2b^2/6)} \times \left[1 - \frac{P_1}{N\exp(-h^2b^2/6)}\right] \qquad \text{(A1.17)}$$

For $N \ll 1$ and $h^2b^2/6 \ll 1$ one has

$$\frac{P_1}{N} = \frac{1-\exp(-h^2b^2N/6)}{h^2b^2N/6} = \frac{1-\exp(-V)}{V} \qquad \text{(A1.18)}$$

$$\frac{P_2}{N} = \frac{2}{V^2}(V - (1-\exp[-V])) \qquad \text{(A1.19)}$$

Thus

$$P(h) = \frac{2}{fV^2} \times \left[V - (1-\exp[-V]) + \frac{f-1}{2}(1-\exp[-V])^2\right] \qquad \text{(A1.20)}$$

where

$$V = b^2Nh^2/6 = \left(\frac{f}{3f-2}\right)\langle S^2\rangle h^2 \qquad \text{(A1.21)}$$

The latter equivalence follows from the equation of the mean square radius of gyration

$$\langle S^2\rangle = \frac{3f-2}{f}N \qquad \text{(A1.22)}$$

Appendix 2

Derivation of M_w, M_n, $\langle S^2\rangle_z$, and $P_z(h)$ for the Nonrandom AB$_f$ Polycondensates. Following the procedure of cascade theory as outlined in ref 8 and 9 one finds for the link probability generating functions of units in the zeroth and nth generation of the molecule represented as a rooted tree

$$F_0(\mathbf{s}) = (1-\alpha+\alpha s_b)(1-\beta+\beta s_a)^f \qquad \text{(A2.1)}$$

$$F_{na}(\mathbf{s}) = (1-\beta+\beta s_a)^f \qquad \text{(A2.2)}$$

$$F_{nb}(\mathbf{s}) = (1-\alpha+\alpha s_b)(1-\beta+\beta s_a)^{f-1} \qquad \text{(A2.3)}$$

In these equations α and β are the link probabilities for a reaction of a group A and B, respectively, f is the number of B groups per monomer unit, and $\mathbf{s} = (s_a, s_b)$ is the vector of auxiliary functions which indicate reactions with A or B groups, respectively.

Performing the cascade substitution one obtains the path weighted generating function $U_0(\mathbf{s})$ in which ϕ_n are weighting functions to be specified below which depend on the generation number

$$U_0(\mathbf{s}) = s^{\phi_0}(1-\alpha+\alpha U_{1b})(1-\beta+\beta U_{na})^f \qquad \text{(A2.4)}$$

$$U_{na}(\mathbf{s}) = s^{\phi_n}(1-\beta+\beta U_{n+1,a})^f \qquad \text{(A2.5)}$$

$$U_{nb}(\mathbf{s}) = s^{\phi_n}(1-\alpha+\alpha U_{n+1,b}) \times (1-\beta+\beta U_{n+1,a})^{f-1} \qquad \text{(A2.6)}$$

Differentiation at $\mathbf{s} = 1$ yields after some rearrangements

$$U_0'(1) = \phi_0 + 2\alpha\sum_{n=1}^{\infty}\alpha^{n-1}\phi_n + \alpha\beta(f-1)\sum_{n=1}^{\infty}\alpha^{n-1}\sum_{k=1}^{\infty}\alpha^{k-1}\phi_{n+k} \qquad \text{(A2.7)}$$

Special averages are obtained from this general relationship by specifying ϕ_n.[8-10]

Molecular Weights. $U_0(1) = M_w$ if $\phi_n = M_0$

$$M_w = M_0\frac{1-\alpha^2/f}{(1-\alpha)^2} \qquad \text{(A2.8)}$$

where M_0 is the molecular weight of the monomer unit and use was made of the constraint

$$\alpha = f\beta \qquad \text{(A2.9)}$$

The number average molecular weight follows from a relationship by Gordon[38,39]

$$M_n = M_0\frac{2}{2-F_0'(1)} \qquad \text{(A2.10)}$$

$$M_n = M_0(1-\alpha)^{-1} \qquad \text{(A2.11)}$$

Particle Scattering Factor. $U_0'(1) = M_wP_z(h)$ if $\phi_n = M_0\exp(-b^2h^2/6)^n$

$$P_z(h) = \frac{(1-\alpha)^2}{1-\alpha^2/f}\frac{1-(\alpha^2/f)\exp(-b^2h^2/3)}{[1-\alpha\exp(-b^2h^2/6)]^2} \quad \text{(A2.12)}$$

where b is the effective bond length and $h = (4\pi/\lambda)\sin\theta/2$.

Mean Square Radius of Gyration. The mean square radius of gyration may be found from the power expansion of the particle scattering factor

$$P_z(h) = 1 - \tfrac{1}{3}\langle S^2\rangle_z h^2 + \ldots \quad \text{(A2.13)}$$

Expansion of eq A2.12 gives

$$P_z(h) = \left(1+\frac{\alpha^2/f}{1-\alpha^2/f}b^2h^2/3\right) \Big/ \left(1+\frac{\alpha}{1-\alpha}b^2h^2/6\right)^2 \quad \text{(A2.14)}$$

and

$$P_z(h) = 1 - \left(\frac{\alpha}{1-\alpha} - \frac{\alpha^2/f}{1-\alpha^2/f}\right)b^2h^2/3 + \ldots \quad \text{(A2.15)}$$

Hence

$$\langle S^2\rangle_z = b^2\left(\frac{\alpha}{1-\alpha} - \frac{\alpha^2/f}{1-\alpha^2/f}\right) \quad \text{(A2.16)}$$

Since $\alpha \simeq 1$ eq A2.14 can be written as

$$P_z(h) = (1 + \langle S^2\rangle h^2/6)^{-2} \quad \text{(A2.17)}$$

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(40) For a broken rod model, for instance, the length of the rodlike sections must be $\langle S^2\rangle_{\rm rod}^{1/2} = L_{\rm rod}/(12)^{1/2} < \lambda/20$, i.e., $L_{\rm rod} > 57.2$ nm if the wavelength is λ 330 nm. Thus, a chain with four to five rodlike sections must have dimensions of $\langle S^2\rangle^{1/2} > 100$ nm before the rodlike sections will be detectable by light scattering.

Determination of Macromolecular Structure in Solution by Spatial Correlation of Scattering Fluctuations

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ABSTRACT: I propose a new type of scattering technique which includes measurements of scattering intensities at two angles and accumulates the spatial correlation of fluctuations of elastic scattering from solutions. A theoretical analysis of the proposed method shows that it contains structural information much more detailed than the classical diffuse, orientationally averaged scattering intensity pattern. In principle it approaches the information obtainable from difffraction studies of single crystals. A data acquisition and reduction scheme is described. It solves the coefficients of expansion in spherical harmonics that give the oriented, single-particle scattering intensity pattern. The experimental conditions required to perform the proposed measurements and the resolution limitations are discussed. A simple example is presented as an illustration.

(I) Introduction

X-ray and thermal neutron scattering are among the most direct probes of the atomic structure of molecules. Still, in practice, their use for determination of the structure of macromolecules depends on one hand on the availability of single crystals, or on the other hand one has to suffice with low-angle diffuse scattering from solutions in which the detailed atomic information is obscured by orientational averaging of the scattering pattern, and lower resolution is achieved.

Recent development in scattering experiments incorporating intense x-ray and neutron sources and rapid positional-sensitive detectors makes it possible to record the