

Hyperbranching and Excluded Volume Interactions

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This contribution considers several advanced characterization techniques on the basis of static light scattering and presumes basis knowledge on size excluded chromatography (SEC) and field flow fractionation (FFF).

A short retrospect to the history of light scattering is given as a helpful introduction to the higher complexity of these additional procedures. In the past the literature dealt mostly with the scattering behavior of unperturbed linear chains. However, the determined radius of gyration in a good solvent in dependence of the molar mass clearly indicated a perturbation of the dimensions by excluded volume interactions. This contradiction requires additional measurements a careful analysis for instance of the angular dependence of the scattered light and the concentration dependence. Furthermore the preparation of manifold so-called hyperbranched samples induced a new challenge to deriving adjusted theories and the corresponding interpretation by experimentalists.

1. Introduction

The two field indicated by the title of this short review have not been a topic of intense research in the past. Emphasis was mainly laid on the investigation of linear chains or weakly branched chains because of the high flexibility of polymer chains which made these product attractive as new materials. Branching was known to lead to networks at higher monomer conversion, but the networks should consist of fairly long chains between the crosslinks to keep the high flexibility of the material which now displayed a high elasticity resembling those of natural rubber.

The change of interest to highly branched chains was probably evoked by the demand for drug carriers which requires particle with a large number of external functional groups for reversible binding of the medical samples. Both, the linear chains and especially the branched samples, prepared by common synthesis, possess a broad molar mass distribution which are suspected to reduce the material quality and not being suitable for medical application in a human body. Now the tendency turned towards the effort to develop suitable chemical preparation techniques to reduce the width of the distribution or even to prepare perfectly uniform samples. The latter was finally achieved by completely controlled reactions to obtain dendrimers, i.e. sphere-like samples with perfectly branched shells, up to 6 or even more generations. The control of such perfect synthesis affords much labor and therefore Kim and Webster¹ looked for preparations of highly branched samples which would have not the

perfect shape but still a huge number of functional groups, accessible to further reactions. These samples they denoted as *hyper*-branched leaving open what is meant by *hyper*. This blurred but very attractive denomination stimulated countless types of synthesis to branched samples, but conformational properties remained unpredictable from the synthesis alone.

Already in the beginning of polymer science the investigation of the molar mass distribution by special fractionation techniques became an urgent request. We now dispose over the two almost perfect separation techniques of size exclusion chromatography (SEC) and field flow fractionation (FFF). Both complementary methods allow separation of molar masses from a broad size distribution of polymers, by the on-line application of light scattering record of the refractive index which permits the evaluation of the molar mass within small slices and the mean square radius, if the fractions were sufficiently large in size.

The high quality data obtained by the highly developed instruments are immediately evaluated and are printed by an attached computer. The instruments are easy to handle but it remained a somewhat mystery how these results were obtained, because all the intellectual steps were made by the computer. The experience collected with linear chains still allowed for a reasonable interpretation of the results, but this does not hold for the confusing manifold of different branching structures. In addition the linear chains are known to swell to larger sizes by excluded volume interactions, if dispersed in a good solvent, but little is known on the swelling of branched polymers in good solvents. The new aspects require a profound understanding of the fundamental basis of static and dynamic light scattering. This demand is not an easy topic and becomes apparent if one has a look at the history on the question what is light and what happens if light hits a material.

2. Historical Overview

The following (incomplete) list of outstanding scientists gives an impression of the endeavor to clarify the nature of light and its effects. Since 300 years the intriguing question on the nature of light kept scientists busy. The progress was slow, but it may help us to understand what light scattering means and which conclusions can be drawn.

Christian Huygens	1624-1695
Isaac Newton	1643-1727
John Tyndall	1820-1893
James Clerk Maxwell	1831-1879
Heinrich Hertz	1857-1894
Lord Rayleigh	1842-1919
Albert Einstein	1879-1955

The considerations on light scattering apparently started in the 17th century with Christiaan Huygens.² He formulated the principle:

Huygens principle:

“Every point of material that is hit by light is initiated to emit light of the same wavelength”

Huygens principle is a most valuable starting point for a theory of light scattering, this will be demonstrated somewhat later. Clearly his statement includes the opinion that light consists of waves; but Isaac Newton, like Huygens a scientist in astronomy and founder of basic mechanics, adopted the view that light consists of particles and heavily opposed against Huygens principle. For almost two centuries all further development in the research on the nature of light was considerably impeded by Isaac Newton's³ reputation and paramount scientific work mainly in mechanics.

Experimentalists often do not care much about theories and just try to find what can be observed and measured. Such experimental observations were made by John Tyndall about one hundred years after Newton. He noticed that the trail of light in a slightly turbid colloidal solution is visible and can be detected. He also found that the scattered light is partially polarized and that the magnitude of polarization depends on the angle at which the trail of light is envisaged.

An incisive progress in theory was achieved by the ingenious work of James Clerk Maxwell⁴ on the correlation between electricity and magnetism which was compatible to electromagnetic waves, thus giving support to light as electromagnetic waves. Lord Rayleigh⁵ took up this conjecture and derived with Maxwell's theory a first analytic equation for the scattered light from gas molecules. Scattering is assumed to be caused by a primary beam to initiate dipole vibrations of the electrons in the outmost shell in the Nils Bor-model. In theories the expression of polarizability is the amount of vibrating dipoles per unit volume.. In his first draft of the theory Lord Rayleigh he took account only of these dipole vibrations, which already allowed him to explain the blue color of the sky. Einstein⁶ noticed that with this originally drafted equation applied to solutions the *square* of the molar mass, M^2 , of the dissolved particles would result in contrast to expectations. He brought to attention that besides the dipole fluctuations the *local fluctuations in concentration* have to be taken into account. With this correction the molar mass of the particle was correctly obtained.

3. Osmotic compressibility or osmotic modulus.(Debye's contribution)⁷.

Einstein's comment was still incomplete because he considered only the *entropic* part of the fluctuations which neglects the energetic of interactions between particles at finite concentration. Einstein's comment was a result of his work on Brownian motions⁶ and it remains valid only at infinite dilution. Application of Einstein's version to real experiments apparently leads to molar masses which decrease at higher concentration. Debye and one year later Zimm, Stein and Doty⁸ took up this topic and repeated Einstein's calculation but now using the chemical potential rather than only the entropy of the concentration fluctuations. The chemical potential $\partial G / \partial n_{particle}$ in turn is related to the osmotic pressure caused by the dissolved molecules, and with this expansion of Einstein's derivation the following equation for scattered light was obtained.

$$\frac{i(\theta)}{I_0} r^2 = R_\theta = \frac{4\pi^2}{\lambda_0^4 N_a} \left[\left(\rho \frac{\partial n}{\partial \rho} \right)^2 RT \beta + \left(n_0 \frac{\partial n}{\partial c} \right)^2 cRT \frac{\partial c}{\partial \Pi} \right] \quad (1)$$

The Rayleigh ratio $R_\theta = \frac{i(\theta)}{I_0} r^2$ takes into account that the scattered intensity $i(\theta)$ decreases with the square of the distance to the detector from the scattering volume. I_0 denotes the primary beam (which is about 10^6 times stronger than the scattering intensity $i(\theta)$).

The first part in eq.1 is related to the *isothermal* compressibility β of the solvent (which is very low for pure liquids) and the second part is related to what may be denoted as *osmotic* compressibility which is a much more pronounced effect than the isothermal compressibility and is strongly related to the value of the molar mass.

The effect of osmotic compressibility requires some additional comments. Due to thermal fluctuations (i.e. Brownian motions) a local increase or (decrease) of the concentration, around average concentration occurs. These deviations from equilibrium cause an increase (or decrease) of the osmotic pressure which tends to push this micro heterogeneity back to equilibrium; The back-driving force is much weaker and allows for considerably larger deviations from equilibrium compared to the force in the *density* fluctuations.

It is sensible to subtraction the scattering intensity of the solvent because we are especially interested in the behavior of the dissolved polymers. After subtraction of the separately measured scattering intensity of the solvent the now well known Debye⁹ equation is obtained.

$$\Delta R_{\theta} = \frac{4\pi^2}{\lambda_0^4 N_A} \left(n_0 \frac{\partial n}{\partial c} \right)^2 c \frac{RT}{(\partial \Pi / \partial c)_{T,p}} = Kc \frac{RT}{\partial \Pi / \partial c} \quad (2)$$

with

$$K = \frac{4\pi^2}{\lambda_0^4 N_A} \left(n_0 \frac{\partial n}{\partial c} \right)^2 \quad (3)$$

Even with this simplified writing eq.(2) is inconvenient if used for the analysis of measurements because the important quantity which contains the molar mass is enclosed in the osmotic pressure. Therefore Debye⁹ suggested to use the reciprocal of eq.(2)

$$\begin{aligned} \frac{Kc}{\Delta R_{\theta}} \frac{1}{RT} \frac{\partial \Pi}{\partial c} &= \frac{1}{M_w} + 2A_2c + 3A_3c^2 + \dots \\ &= \frac{1}{M_w} [2A_2M_w c + 3A_3M_w c^2 + \dots] \equiv \frac{1}{M_{app}(c)} \end{aligned} \quad (4)$$

In this equation $A_2; A_3 \dots A_n$ are the *second, third* and *nth* virial coefficient in the power expansion of the osmotic pressure in terms of concentration. Eq.(4) remains valid if the dimension of the dissolved samples are small compared to the wavelength of the light, more precisely if the radius of gyration $R_g < \lambda/20$ (e.g. if the red light of an HeNe laser is used R_g should be smaller than 10 nm.). For larger macromolecules or colloid particles an angular dependence of the scattered light occurs. These angular dependencies allow for the determination of R_g and for large structure in the range of the wavelength this angular dependence is characteristic for special structure (rods, sphere or coiled macromolecules) and will be discussed in the next section.

4. Additional remarks on the Osmotic Compressibility or the Osmotic Modulus

4.1 Coil-Coil Interpenetration Function

The second virial coefficient is known to indicate the solubility of the dissolved polymer in a solvent. i.e. a large value indicates good solvent behavior and a value of $A_2 = 0$ a quasi ideal solution, denoted by Flory as theta θ -solvent. At the temperature $T=\theta$ of the used solvent the repulsive and attractive forces are balanced to zero. Also negative values are possible but eventually lead to phase separation into a polymer-rich and polymer-low concentration. For flexible polymers A_2 is given by the equation¹⁰

$$A_2 = 4\pi^{3/2} N_A \frac{R_g^3}{M^2} \Psi^* \quad (5)$$

N_A is Avogadro's number, R_g the radius of gyration and Ψ^* the asymptotic penetration function at large molar mass of the sample. Eq.5 resembles the van der Waals equation for real gases with the exception of the numerical factors and the use of the cube of the radius of gyration instead of the radius of an equivalent hard sphere, but it differs significantly by the additional penetration factor Ψ^* . This mathematically rather complex function has a simple meaning: Polymers have no defined surface but consist of flexible chain ends which partially are stretched out. If two such polymers are coming into contact the dangling chain segments from both particles will penetrate and form a common domain. The depth of penetration depends on the strength of the repulsive interactions between the various repeat units of the two interacting particles which this is given by the excluded volume β of the individual monomer repeat units. Figure 1 may illustrate what is meant.

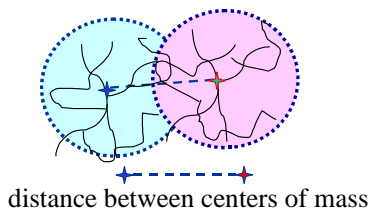


Figure 1: Sketch of two interpenetrating macromolecules.

A small Ψ function correspond to deep penetration and depends to some extent on the molar mass of the sample and soon with increasing M reaches a limited value of $\Psi^* = 0.29$ ^{11,12} for flexible linear chains. As may be expected this penetration function depends on the molecular structure. Figure 2 shows this behavior for a number of examples.¹³

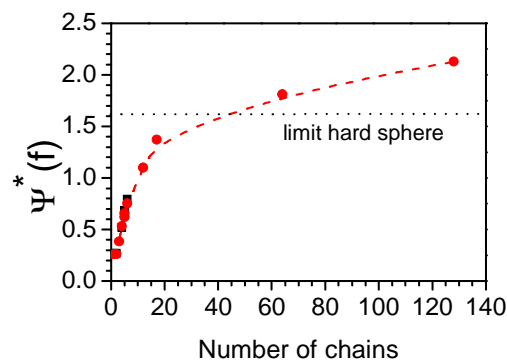


Figure 2: Penetration functions of linear and star-branched polymers, mainly from star-molecules. The two points with more than 100 chains refer to star-microgels. i.e. with a small microgel as core. For further references see ¹³4.2 Overlap Concentration and Entanglement

Further insight in the inter-particle interactions is obtained if eq.5 is slightly rearranged by multiplying it by M

$$A_2 M = (4\pi^{3/2} N_A \Psi^*) \frac{R_g^3}{M} \equiv \frac{1}{c^*} \quad (6)$$

where c^* may be taken as the weight concentration of the monomer repeat units in the particle.

Let us shortly consider the ratio c/c^* : We can make measurements at $X = c/c^* < 1$ or at $X = c/c^* > 1$. We then notice that at $X=1$ the concentration of monomer units in the dissolved particles equals the in-weight concentration. In other words the macromolecules must just attach each other, and at higher concentration $X > 1$ the segment clouds of the chain must start to overlap and form an dynamic network of entangled chains. Thus c^* may be called the *overlap concentration*.

With this notation eq.(4) can be written¹³

$$\frac{M}{RT} \frac{\partial \Pi}{\partial c} = [1 + 2A_2 M c + 3A_3 M c^2 + \dots] = 1 + 2X + 3g_3 X^2 + 4g_4 X^3 + \dots \quad (7)$$

This notation goes back to Pierre-Gilles de Gennes.¹⁴ It was known to him that for hard spheres the higher virial coefficients can be expressed in terms of A_2 , and this was possible for other uniform structures.

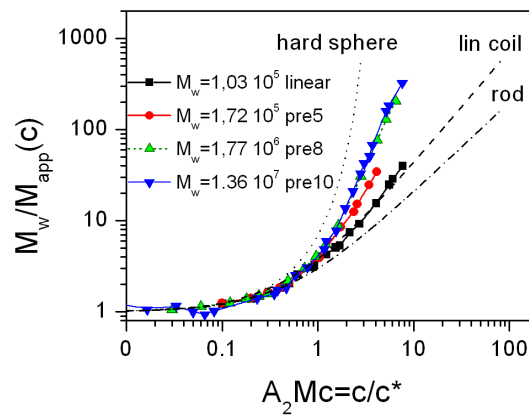


Figure 3: Variation of the osmotic modulus $(M_w / RT)(\partial \Pi / \partial c) = M_w / M_{app}(c)$ as a function of c/c^* for three models and experimental data from a linear polyester and three crosslinked polyesters of the same chain-length.

A well defined interaction curve is obtained, but with different coefficients g_n for linear or branched structures. Against de Gennes expectation differences between different structures

of the dissolved particles are noticeable, without knowing the mean square radius of gyration. Eq.7 is of great value for instance, if soft materials are characterized by rheology, since at $X > 1$ an *entangled network* can be formed which exhibits special behavior in the rheological experiment. Figure 3 shows some examples of the osmotic modulus and the theoretical curves, i.e. for hard spheres¹⁵, cylindrical structures¹⁶ and flexible coils.¹⁷ The graphs elucidates whether a flexible or a stiff chain is in the solution or whether the particle had a more globular shape.

5. Angular dependence of scattered light

It was already mentioned that the scattering function of eq.4 or 7 holds only for small particles compared to the used wavelength. Macromolecules with radii of gyration larger than 10 nm cause an angular dependence which is described by a normalized function $P(q)$

$$P(q) \equiv \frac{i(\theta)}{i(\theta = 0)} \quad (8)$$

The required extension of eq.4 is given by

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{MP(q)} + 2A_2c + 3A_3c^2 + \dots \quad (9)$$

This angular dependence of the scattering intensity at large q -values displays a characteristic behavior and is for this reason called particle scattering factor or molecular structure factor. To understand this one has to go to some details on the interference of the scattering waves if two scattering points are separated by a certain length, for instance, these may be the two end-points of a segment in a chain-molecule. Figure 4 may demonstrate on a simple example when only two such scattering points are activated as scattering emitters. Because of the finite distance length between these points a phase difference between the two light waves arises and causes interference. The phase difference increases with the scattering angle. The effect can be described by unit vectors of the primary beam and from the scattered light. The magnitude of the difference of the two unit-vectors is given by $[\mathbf{s}_0 - \mathbf{s}] = 2 \sin(\theta/2)$, and when the wave length of the used light is taken into account one obtains for the magnitude of the *scattering vector* \mathbf{q}

$$[q] = q = \frac{4\pi n_0}{\lambda_0} \sin(\theta/2) \quad (10)$$

Note, the scattering vector has the dimension of 1/length.

In a real experiment the macromolecules are composed of many chain segments of different length, and therefore the sum over all pairs of units which form covalently bond segments has to be taken. An example of such segment is shown in Figure 4b. The summation finally leads, after normalization by the total number of units, to eq.11 for the particle scattering factor

$$P(q) = \frac{1}{N^2} \sum_{j=1}^N \sum_k^N \left\langle \frac{\sin(qr_{jk})}{qr_{jk}} \right\rangle \quad (11)$$

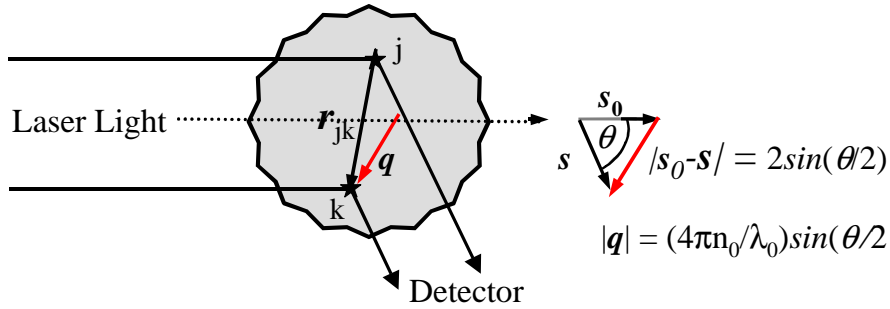


Figure 4a: The set-up of the primary light beam and the position of the detector for detection of the scattered light at angle θ . The insert to the right indicates the definition of the scattering vector q .

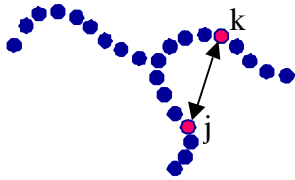


Figure 4b: Demonstration of the distance vector between two units j and k in a branched chain. The segment contour length consists in this case of 9 repeat units and a contour length of $l_{jk}=8b$

Eq. 11 contains the average $\langle \sin(qr_{jk})/qr_{jk} \rangle$ which requires some additional comments.

(i) *Orientalional fluctuation*: The derivation of $\sin(\mathbf{q}\cdot\mathbf{r})/(\mathbf{q}\cdot\mathbf{r})$ was not a trivial task. It takes account of the fact that due to Brownian motions the subject can take all orientations. In experiments we measure the *average* over all orientations. The $\sin(qr_{jk})/qr_{jk}$ function arises from the average of a cosine function with an argument that contains the cosine of the angle between the orientation of the distance vector \mathbf{r} and the scattering vector \mathbf{q} (see Figure 4a).

$$\langle \cos(\mathbf{q}\cdot\mathbf{r}) \rangle = \frac{1}{qr} \int_0^{qr} \cos(u) du = \frac{\sin(qr)}{qr} \quad (12)$$

(For details of the not trivial derivation see the original paper by Debye¹⁸ and the repeat by Guinier¹⁹ .

(ii) *End-to-end fluctuations*: For rigid particles like hard spheres or rigid rod no further derivations are required, but for flexible linear or branched chains the end-to-end distance of the two segment ends fluctuate around an average length. This average is indicated by the $\langle \dots \rangle$ brackets and requires the knowledge of the end-to-end distance distribution. The adequate distributions are often not known, and approximations have to be used.

Once the average $\langle \sin(qr_{jk})/qr_{jk} \rangle$ has been derived the sum in eq.11 over all pairs of repeat units has to be performed (Huygens principle). For a few special structures this double sum can fairly easily be evaluated or replaced by integrals. Such calculations were made already soon after the basic Lord Rayleigh's equation²⁰ and he was the first one who derived the scattering function of uniform hard spheres. About 30 years later similar derivations were performed for infinitely thin rods of defined length by Neugebauer²¹ and for coiled and uniform linear chains by Debye²².

The following three equations for the three idealized models are specially useful because they correspond to structures with three fractal dimensions d_f : $d_f=3$ for hard spheres, $d_f=2$ for a linear random coil, and $d_f=1$ for rigid rods. In real experiments the behavior of dimensions lies in between these three examples. e.g. a $d_f=1,7$ for linear chains in a good solvent is obtained but in a θ -solvent the corresponding value is $d_f=2$ (which looks like an Euclid dimension of a planar structure; but the random coil is a statistical structure).

$$P(qR)_{hard\ sphere} = \left(\frac{3}{(qR)^3} \right)^2 [\sin(qR) - qR\cos(qR)]^2 \quad \text{Lord Rayleigh}^{20} \quad 1914 \quad (12)$$

$$P(qL)_{rod} = \frac{2}{qL} \left[Si(qL) - \left(\frac{\sin(qL/2)}{qL/2} \right)^2 \right] \quad \text{Neugebauer}^{21} \quad 1943 \quad (13)$$

$$P(qR_g)_{random\ coil} = \frac{2}{(qR_g)^4} \left[(qR_g)^2 - 1 + \exp(-(qR_g)^2) \right] \quad \text{Debye}^{22} \quad 1945 \quad (14)$$

in eq.12: $R = \sqrt{(5/3)R_g^2}$ is the radius of the sphere;

in eq. 13: $L = \sqrt{12R_g^2}$ is the length of the infinitely thin rod;

in eq. 14: $(R_g)^2 = (R_N)^2/6$ is the mean square radius of gyration of the random coil.

These particle scattering factors are well known and give a good orientation over the manifold difference of particle scattering factors from linear and branched structures.

The functions of the three particle scattering factors in eq.12-14 are presented in varying plot types (Figures 5a-c) which have special advances or weaknesses, but all demonstrate that these three models allow conclusions whether a fairly stiff sample, or a branched one and the linear coil in between are causing this special behavior.

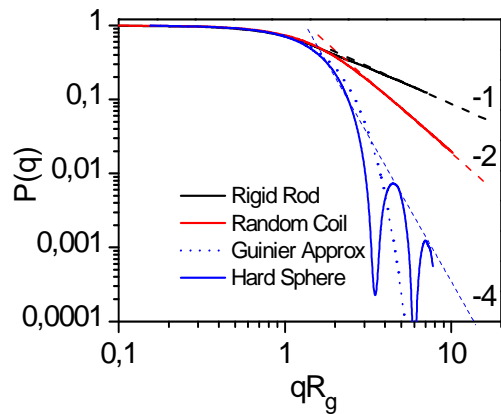


Figure 5a: log-log presentation the negative digits denote the slope.

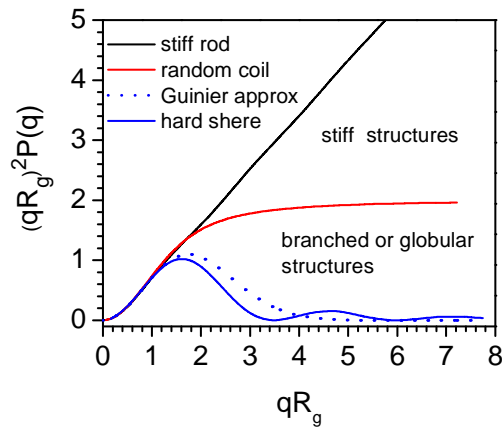


Figure 5b: Kratky plot presentation.

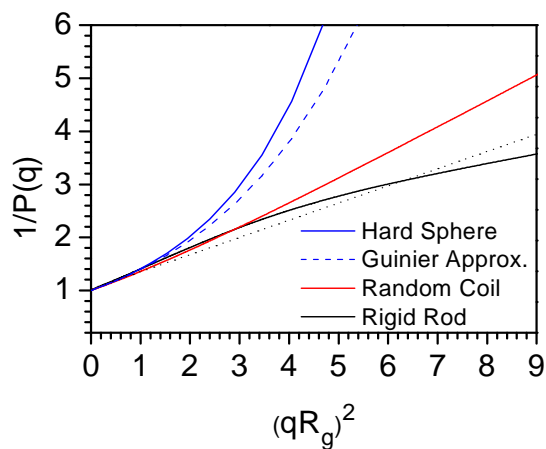
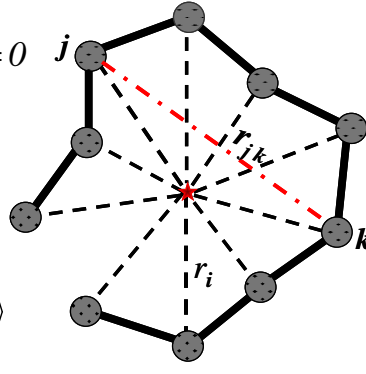


Figure 5c: Zimm plot representation

In these plots the product qR_g was used instead of the scattering angle θ or the magnitude of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$. The qR_g product has no dimension and therefore allows for a unproblematic comparison of results obtained in other laboratories or by use of a different equipment.

Mean Square Radius of Gyration $\langle R_g^2 \rangle$

In all these graphs the radius of gyration occurs as a sensible scaling factor, and indicates the outstanding significance of this parameter: This fact arises the question how R_g is defined and how it can be measured and predicted by theory? Figure 6 shows as an example a simple sketch of a chain model.



$$\langle \mathbf{R}_g \rangle = \sum_{i=1}^N \mathbf{R}_i = 0$$

$$\langle r_{jk}^2 \rangle = \langle (R_j - R_k)^2 \rangle$$

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^N \langle r_i^2 \rangle$$

$$\langle R_g^2 \rangle = \frac{1}{2N} \sum_{j=1}^N \sum_{k=1}^N \langle r_{jk}^2 \rangle$$

Figure 6: Model for a short chain demonstrating the position of the central point of inertia, the corresponding vectors from this center to the various monomer units, and the vector between two points of segment length (broken red lines). The equations around this cartoon define the various sums between the chain units. (See text for further information).

The broken lines in his figure illustrates the various vectors pointing towards the center of mass (indicated by the red star). This center in turn is defined by the condition that the sum over all vectors \mathbf{r}_i from this point to the various mass centers of the particle should be $\sum_{i=1}^N \mathbf{r}_i = 0$. However, the *magnitude* of the individual vectors are finite and the square of them is positive. Accordingly the mean square radius of gyration is defined by the square

$$\langle R_g^2 \rangle = \frac{1}{N} \sum_{i=1}^N \langle r_i^2 \rangle \quad \text{mean square radius of gyration} \quad (15)$$

This equation contains the average brackets $\langle \dots \rangle$ which indicate that the definition also holds if the segment length fluctuates around an average value. If flexible segments are considered the center of mass is not positioned on one of the repeat units but somewhere between the segment clouds. This means eq.15 cannot directly be applied.

Zimm and Stockmayer²³ noticed that the position of the center of mass can be eliminated and replaced by the sum over all of the N^2 vectors \mathbf{r}_{jk} with the result

$$\langle R_g^2 \rangle = \frac{1}{2N} \sum_{j=1}^N \sum_{k=1}^N \langle r_{jk}^2 \rangle \quad (16)$$

A short outline of this derivation is the following:

- (1) One can form a vector sum starting in Figure 6 with the center of mass, going to the unit 1 and forwards step by step to the unit N .
- (2) The same vector sum can be formed if the first vector from the center goes to the unit 2 from there to unit N and finally from there to the unit 1 and the same can be done with the first vector going to the unit i .
- (3) Now the sum over all these vector sums can be formed, which (by definition of center of mass) is 0 because positive and opposite vector directions occur with the same frequency ; but the square over the double sum in eq.16 remains positive.
- (4) In the double sum of eq.16 represents the summation from j to k but also from k to j , but both procedure give the same result, in other words the mean square radius is counted twice. Therefore the double sum has to be divided by 2.

7. The forceful impact to the light scattering theory by Bruno H. Zimm (1920-2005)

As shown already in eq.11 the sum over the $\sin(x_{jk})/x_{jk}$ has to be performed and allowed prediction on the particle scattering behavior. This task is easy if a Gaussian conformational distribution is used. In this case a fairly simple result is obtained if the Debye approximation is applied. This approximation corresponds to a linearization of the exponential function $\exp(-ax_{jk}^2) \approx 1 - ax_{jk}^2 + \dots$ which of course should be applied only after an exact solution has been derived. The exact derivation leads even for the Gaussian approximation to rather complex functions and one has to take much care to check the limits of the approximation. Certainly the first member is well known and leads for the particle scattering function to

$$P(q) \approx \left(1 - \frac{q^2}{6N^2} \sum_j^N \sum_k^N \langle r_{jk}^2 \rangle + \text{higher terms of } q^{2n} \right) = 1 - \frac{1}{3} \langle R_g^2 \rangle q^2 + \dots \quad (17)$$

With eq.(16) one immediately obtains for the initial slope in a plot $P(q)$ against q^2 the mean square radius of gyration without knowing anything of the actual conformation. In other words *the radius of gyration is an **universal** parameter.*

The first derivation of the scattering function for linear polymers of uniform contour length $L = bN$ was made by Debye²² on the basis of unperturbed dimensions with b the bond length and N the number of repeat units in the chain. The simple expression of eq.14 was obtained under the assumption of $b/N \ll 1$, which is an excellent approximation in common static light

scattering. So far the derivations of the particle scattering factors of eqs12-14 remained essentially a sheer theoretical task and was not directly linked to the chemistry of preparation.

This attitude changed in 1948 with the famous two papers in *J. Chem. Phys* by B. H. Zimm.²⁴

The following few remarks give in short an appreciation of his work as an outstanding scientist. Bruno Zimm set marks in the three different fields:

- (1) In the physics of static light scattering from linear and branched chains as a theoretician and an experimentalist (Cooperation with Stockmayer²³);
- (2) In the field of biophysics by the theory of helix-coil transition of proteins²⁵ and
- (3) In hydrodynamics by the contribution of draining to the intrinsic viscosity from linear chains and the effect on branched polymers.²⁶

The connection to realistic structure as prepared by chemists was achieved by combination of Debye's derivation of eq.14 and Flory's²⁷ most probable molar mass distribution with the result

$$P(q)_{polydisperse\ coil} = \frac{1}{1 + (1/3)R_g^2} \quad (18)$$

He also extended these calculation to linear chains with a distribution which corresponds to *m*-end-to-end coupled linear chains (Schulz distribution²⁸) thus showing that the angular dependence of the scattered light is modified by the molar mass distribution.

8. Two new fields in science on polymer conformations

These two fields are

(8a): The understanding of the polymer conformations perturbed by *excluded volume interactions* and (8b) The preparation of *hyper-branched polymers* and prediction of their conformational properties.

Some detail of the out-coming new demands are given in the following two sections.

8a: Conformation properties of linear polymers under the influence of excluded volume interactions.

Chain expansion and radius of gyration

Since the work by Kirkwood and Riseman²⁹ on the intrinsic viscosity it was known that in good solvents a swelling of the dimensions occurs which is caused by the finite volume of the individual repeat units and weak attraction interaction among the units in the chain. Also it

was observed that the swelling slightly increased with the degree of polymerization. Flory presented a theory that could describe these features of swelling by an expansion factor $\alpha = R_g / R_{g0}$ in which the index zero refers to the unperturbed chain. The derived equation was³⁰

$$\alpha^5 - \alpha^3 = 2.6z; \quad z = \left(\frac{3}{2}\right)^{3/2} \frac{\beta}{b^3} N^{1/2} \quad (19)$$

For large degrees of polymerization the effect of α^3 compared to α^5 can be neglected. With the definition of α and $R_{g0} \propto N^{0.5}$ one obtains for the swollen chain

$$\langle R_g^2 \rangle \propto N^{1+\varepsilon} \quad \text{with } \varepsilon = 0.2; \quad \text{or } R_g = KN^\nu \quad \text{with } \nu = 0.6 \quad (20a,b)$$

This relationship was criticized for several years, but after the comprehensive self-avoiding random walk simulations by Domb et al.³¹ nearly the same result was obtained with the slightly smaller value of the exponents $\varepsilon = 0.176$ or $\nu = 0.588$. With these data the mean square radius of gyration of the expanded random coil was calculated by Peterlin³² to be

$$\langle R_g^2 \rangle = b^2 \frac{N^{2\nu}}{2(1+2\nu)(1+\nu)} = b^2 \frac{N^{1.176}}{6.911} \quad \text{for } \nu = 0.588 \quad (21a)$$

$$\langle R_{g0}^2 \rangle = b^2 \frac{N}{6} \quad \text{for } \nu = 0.5 \quad \text{unperturbed chain} \quad (21b)$$

Comment on approximations

Eq. 20a describes the asymptote for large chain molecules in a good solvent and represents the upper limit. In several solvents this limit is not observed in experiments but the radius of gyration of long chain molecules can still be described by power law behavior with exponents of $0.500 \leq \nu \leq 0.588$ where $\nu = 0.500$ refers to the theta solvent and unperturbed conformations and $\nu = 0.588$ for good solvents. At present only the good solvent behavior has been considered and scaling behavior is assumed to be valid also for short chains or segment lengths. These approximations have been used also for the segments in branched chain molecules. The results obtained by present theories give a much better agreement with experimental findings, but small deviations can be expected. A further improvement is obtained by interpolation between the unperturbed and fully perturbed behavior.

Hydrodynamic radius

In contrast the hydrodynamic radius R_h defined by the Stokes-Einstein relationship and the diffusion coefficient D

$$D_0 = \frac{kT}{6\pi\eta_0} \left\langle \frac{1}{R_h} \right\rangle \quad (22)$$

cannot be derived in a similar manner as shown for the radius of gyration. For unperturbed conformation the common Gaussian size distribution for segments of n units is known

$$W(X, n) = \left(\frac{3}{2\pi} \right)^{3/2} \exp\left(-\frac{2}{3} X^2\right) 4\pi X^2 dX; \quad X = R/R_n \quad (23)$$

with R_n as the end-to-end distance of a chain with n repeat units, and R the variable.

The inverse hydrodynamic radius of a chain of n units is¹⁰

$$\left\langle \frac{b}{r_n} \right\rangle_0 = \left(\frac{6}{\pi} \right)^{1/2} n^{-1/2} \quad (24)$$

For the perturbed dimensions the required distribution was derived by Domb et al.³¹ from self-avoiding random walk simulations³³

$$(X, n) = 0.279 X^{0.28} \exp\left(-\frac{6}{5} X^{-2.43}\right) 4\pi X^2 dX; \quad X = R/R_n; \quad R_n = bn^{0.588} \quad (25)$$

With this distribution the average of the inverse hydrodynamic radius of a segment is³⁴

$$\left\langle \frac{b}{r_h} \right\rangle = \left(\frac{5}{\pi} \right)^{1/2} \frac{1}{0.582n^{0.588}} \quad (26)$$

To obtain the hydrodynamic radius of the total linear chain with N repeat units the results from eq.24 and eq25 have to be summed over all segment pairs in the macromolecule with the results^{32,34}

$$\left\langle \frac{b}{R_{h0}} \right\rangle = \left(\frac{6}{\pi} \right)^{1/2} \frac{\sum_1^N (N-n)n^{1/2}}{\sum_1^N (N-n)} = \left(\frac{6}{\pi} \right)^{1/2} \frac{8}{3} N^{-1/2} = 3.6843 \times N^{-0.5} \quad \text{unperturbed} \quad (27a)$$

$$\left\langle \frac{b}{R_h} \right\rangle = \left\langle \frac{5}{\pi} \right\rangle^{1/2} \frac{\int_1^N (N-n)n^{-0.588} dn}{\int_1^N (N-n)db} = \left\langle \frac{5}{\pi} \right\rangle^{1/2} \frac{3.4378}{N^{0.588}} = 4.323 \times N^{-0.588} \quad \text{excl.vol.} \quad (27b)$$

For the ratio $R_g/R_h \equiv \rho$ one has with $R_{g0} = b(N/\sqrt{6})$ and $R_g = bN^{0.588}/\sqrt{6,911}$ for the unperturbed and perturbed radii of gyration³⁴

$$\rho_0 = 1,504 \text{ for the unperturbed linear chain} \quad (28a)$$

$$\rho = 1.651 \text{ for the chain with excluded volume} \quad (28b)$$

The ρ parameter is a valuable quantity because it gives significant information on the effects of branching.

Influence of excluded volume interaction on the scattering behavior

The effect of excluded volume interactions on the scattering function remained an unsolved issue for a long time because with the distribution of eq.25 the required integral for the average in eq.29 could not be solved analytically.³⁵

$$\phi_{q,n} = \left\langle \frac{\sin(qr)}{qr} \right\rangle = \int_0^{\infty} W(r) \frac{\sin(qr)}{qr} 4\pi r^2 dr \quad (29)$$

This integral is easily performed if unperturbed chains are considered which are described by the Gaussian distribution of eq. 23 with the result

$$\phi_{q,n} = \exp(-(bq)^2 n) \quad \text{unperturbed chains} \quad (30)$$

For the swollen chains caused by the excluded volume interactions we carried out a numerical integration.³³ The result could be approximated by

$$\phi_{q,n,ex.vol.} \cong \exp - \left[(bq)^2 \left(n^{0.588} \right)^{2.18} / 6.2 \right] \quad (31)$$

According to eq.11 the sum over all pairs of repeat units in eq.31 has to be performed. For uniform linear chains with a fixed length of N repeat units the double sum can be rearranged to a single integral. Furthermore the sum can be well approximated by an integral.

$$P(q) = \frac{1}{N} + \frac{2}{N^2} \int_0^N \phi_{qn,ex.vol.} dn \quad (32)$$

Again this integral cannot be solved analytically but it could be solved by numerical integration. The integration of eq.29 for unperturbed chains is easily performed, all occurring integrals are well known, and the particle scattering factor of eq.14 for unperturbed linear chains is obtained. Figure 7a,b show the derived q -dependence of the particle scattering factor. Clearly only in a limited q -regime the expected fractal behavior is obtained. From the experimental data it will become difficult to determine the right value for the linear slope, i.e.

the fractal dimension. The curves show two further important facts: (i) Up to $qR_g \approx 1.5$ no differentiation between different structures or conformation can be made. In other words the mean square radius of gyration fully dominates the scattering behavior. For linear polystyrene this requires molar masses larger than $M_w > 10^7$ g/mol before deviations become noticeable, and indeed our recent measurements gave clear indications to the onset of perturbed conformations³⁷

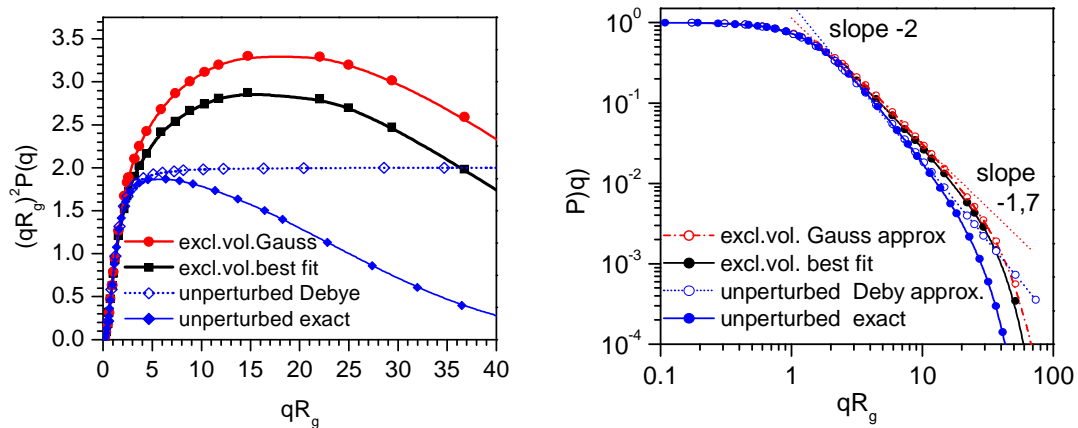


Figure 7 (left) shows the result in form of a Kratky plot. Four curves are presented. (a) the black curve with square symbols indicates the perturbed linear chain by excluded volume interactions; (b) the blue dotted line and the open routs refers to the unperturbed chain with Debye's approximation and (c) solid blue line with filled symbols the exact solution of the double sum and (d) the result with the Ptitsyn approximation³⁶ in which a Gaussian distribution is used but with the perturbed mean square radius $\langle R_g^2 \rangle = b^2 n^{2\nu} / (1 + 2\nu)2(1 + \nu)$ with $\nu = 0.588$ of the expanded coil. Figure 7 (right) shows the same curves but in the log-log presentation which is preferred in SANS studies.

The domination of the radius of gyration at low qR_g is a fortunate fact for the largely used separation techniques of SEC and FFF,

In these experiments values of $qR_g > 2$ are rarely observed and therefore there is no reason to be worried that special conformational properties would have some influence.

Effects of the statistical nature of chemical reaction

The derived results are applicable to *uniform linear* chains. Such structures can be obtained by living anionic polymerization or by the specific control of enzymes.⁴⁰ These uniform structures appear attractive to chemists but this eagerly followed intention is not supported by

the kinetics of chemical reactions which are described by kinetic velocities. These velocities are averages over a distribution of individual reactions and thus are *statistical* processes. This fact was not immediately clear from reactions between two partners, but the statistical nature of reactions became apparent when polymers were prepared, for instance polyesters. Both, G.V. Schulz²⁸ and P.J. Flory²⁷ realized that predictions on the molar mass can be made only if the molar distribution is known. For linear polymers both scientist independently derived the same distribution which Flory denoted as *most probable* distribution. This distribution is rather common in quite other statistically processes. Much labor and energy has to be invested if for special reasons uniform polymers are required and such structures should be realized. Thus even in biological systems uniform biopolymers are only formed if imperatively needed. Special examples are the huge number of polysaccharides and other more complex structures, (cellulose, pectin, starch, glycogen, collagen, fibrin networks in the blood clotting process and others). With the exception of cellulose all the other quoted examples are branched or form beyond a critical point branching a network.

Branched Polymers

How can structures of branched polymers be predicted from chemical reactions by theory?

This question arose already with the common free radical polymerization of linear chains. Zimm²⁴ used the molar mass distribution of Flory and performed the average of the Debye scattering curve. This technique can in principle be applied to branched samples if the distribution is known but the derivation even for unperturbed chains can become really cumbersome for instance for randomly branched samples using the Stockmayer distribution. Furthermore no extension of this approach to excluded volume interactions appear to be possible.

The Rooted Tree approach

It was Manfred Gordon⁴² in England who in the years around 1960 noticed that the polymer branching very much resembles common family trees if at random any monomer unit of a branched polymer is taken and considered as a root. Of course each family tree is a unique tree, and the same would be the case if it would require to consider trees for every repeat unit that was used as a root. However, we can safely assume that every unit has on average the same reactivity and the rooted tree of our choice corresponds then to a number average. With this mean field approximation the reactivity functional groups on the monomer are actually probabilities of reaction. Figure 8 shows such a rooted tree for a tetra-functional monomer.

In polymer chemistry the presentation of the of repeat units on shells is preferred; but with this picture it becomes increasingly more difficult to verify whether a unit belongs to the n th shell or to shells of numbers $n-1$ or $n+1$. This problem does not occur with the rooted tree presentation. Now the structure of the macromolecules is clearly defined by separated generations and the population of repeat units in these generation.

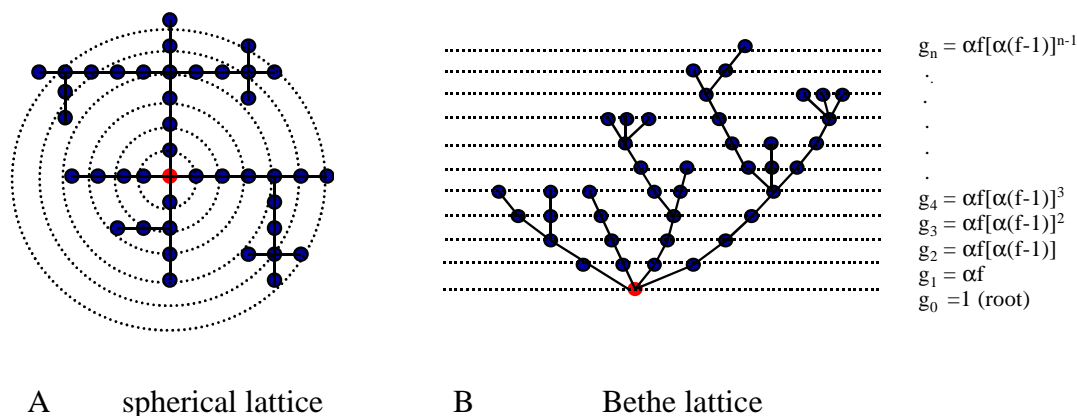


Figure 8: Representation of a branched macromolecule: (A) in form of shells around a selected unit and (B) in form of a rooted tree in which the distance between the n th and $(n+1)$ th generation is uniquely defined by the bond length b .

In this example the number of units linked to this monomer is on average 4α if $\alpha \leq 1$ is the *extent of reaction* of one functional group, or in mathematical terms the *probability of reaction*. These 4α units linked to the root form the first generation. In this generation one of the four functional groups have already been used and therefore only three functional groups remain available to form the population of the second generation, and the same situation remains for the third and all higher generations. In this simple case one needs to know only the simplest rules of combining probabilities⁴⁴ and obtains for the population of monomer units in the n th generation.

$$g_n(\alpha) = 1 + 4\alpha(3\alpha)^{n-1} \quad (32)$$

Clearly, if we form the sum over all generations the weight average degree of polymerization is obtained

$$DP_w = 1 + \frac{4\alpha}{1-3\alpha} = \frac{1+\alpha}{1-3\alpha} \quad (33a)$$

The equation can easily be generalized for monomers with f -functional groups as was done by Stockmayer in 1943⁴³.

$$DP_w = 1 + \frac{f\alpha}{1-(f-1)\alpha} = \frac{1+\alpha}{1-(f-1)\alpha}, \quad W. H. Stockmayer \quad (33b)$$

This equation is remarkable, because it includes with $f = 2$ the behavior of polydisperse linear chains as it was derived 1948 by B.H. Zimm²⁴ with the known molar mass distribution. Remarkably the treatment of rooted trees requires no knowledge of the molar mass distribution. Of course, with more complex branching reactions a more sophisticated algorithm is needed which requires the system of transition probabilities, but even this is fairly simple and it can be learned from the book by William Feller⁴⁴ Moreover also the radius of gyration R_g , the hydrodynamic radius R_h and the and the particle scattering factor $P(q)$ are derived for such polydisperse unperturbed structures.

Perturbation by excluded volume interactions

Valuable insight into the branched structure are gained in particular from the ratio $\rho = R_g / R_h$ which has been recognized as a characteristic parameter for branching.⁴⁵ However, these parameters change their values in good solvents, and further effort has to be invested to extend present theories. For a long time the excluded perturbation could not satisfactorily be solved in particular for the prediction of the angular dependent scattering curves. The available equations for linear chains could not be derived analytically also for the branched structures. We applied numerical integration and could derive numerically the required quantities. A few examples are already published and a more detailed comparison is experimental findings is in progress.

Conclusion remarks

At present the characterization of polymers is made by the highly developed separation techniques. These optimized techniques permit precise determination of the weight average molar mass M_w and the molar mass distribution $w(M)$ and, in addition, often the radius of gyration R_g . The dependence of R_g on the molar mass gives insight on a possible fractal behavior, effects of branching and good solvent behavior. Still for branched polymers the obtained results from these separation techniques do not give sufficient insight and information for a conclusive interpretation of conformational properties. There exist an almost unlimited diversity of branching and more details have to be collected. Mostly the one line detection of the intrinsic viscosity is used. The present understanding of this quantity is based on the so-called universal Kuhn-Mark-Houwink equation which becomes misleading if applied to branched samples.⁴⁶ The simultaneous detection of the radius of gyration *and* the hydrodynamic radius would be a real step forward, but the measurement of dynamic light

scattering requires some recording time, which from streaming sample is not always sufficiently long. The combination of SEC and FFF technique is a well established procedure and these techniques should be combined with other ones. Most promising are SANS but also the method has the draw-back that the radius of gyration is difficult to measure accurately for large particles. Combination with separate static light scattering from *not fractionated* samples will become important. Hopefully a new and very efficient static light scattering device will become available soon on the market.

Appendix: Osmotic modulus derived by theory for three special models

Abbreviation: $X = A_2 M_c c = c / c^*$ scaled concentration;

$$F(c) = \frac{M_{app}(c)}{M_w} = \frac{M_w}{RT} \frac{\partial \Pi}{\partial c} \quad \text{scaled osmotic modulus} \quad (A1)$$

Hard spheres: (Carnahan and Starling)¹⁵

$$F(c) = \frac{1 + 4y(1 + y - y^2) + y^4}{(1 - y)^4}; \quad y = X/4 \quad (A2)$$

Flexible coils of linear chains (Ohta & Oono)¹⁷

$$F(c) = 1 + \frac{1}{8} \left[9X^* - 2 + 2 \frac{\ln(1 + X^*)}{X^*} \right] \exp \left[\frac{1}{4} \left(\frac{1}{X^*} + \left(1 + \frac{1}{X^{*2}} \right) \right) \ln(1 + X^*) \right]$$

$$X^* = \frac{X}{(9/16) - (1/8) \ln(M_w / M_n)}$$

Cylinders of large axial ratio $p = (l / r_c)$, cylinder length (l), cross-sectional radius (r_c):

(Cotter & Martire)¹⁶

$$F(c) = \frac{1 + 2(1 + 1/p)X^* + (2/p)X^{*2}}{(1 - X^*/p)^4}; \quad X^* = \frac{X}{1 + 3/p} \quad (A3)$$

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