

Is the Universal Law Valid for Branched Polymers?*

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In the years between 1908 and 1910 Albert Einstein^[1] derived his famous equation for the increase of the solvent viscosity if spherical particles are added to a liquid. This equation may be written in terms of intrinsic viscosity, but may also be expressed in terms of molar mass and the Avogadro number N_A [Eq. (1); R is the radius of a hard sphere].

$$[\eta] = \frac{\eta_s - \eta_0}{\eta_0 c} = 2.5 \frac{V}{m} = \frac{10\pi}{3} N_A \frac{R^3}{M} \quad (1)$$

Evidently the left and the right sides in Equation (1) have the same dimension, and therefore, the parameter $\Phi_{\text{Einstein}} = 10\pi/3$ is a dimensionless quantity. Several years later, Staudinger noticed that the easily measurable intrinsic viscosity is an excellent quantity to describe solution properties of linear polymer chains using the Flory–Fox equation [Eq. (2); R_g is the radius of gyration].^[2]

$$[\eta] = \Phi_F \frac{R_g^3}{M} \quad (2)$$

In this equation again $[\eta]$ and R_g^3/M have the same dimension, and consequently the Flory parameter Φ_F seems to fulfill the characteristics of a universal quantity, at least for linear chains. Such universality is however questionable as it has been observed that Φ_F slightly decreases if a good solvent is used instead of a poorer solvent, and this decrease is correlated with the increased swelling of the coil chain.^[3] In practice this important observation is often neglected and the original Φ_F parameter is still used for rough characterization of macromolecules and is known as the “universal constant”.

Herein we show in real systems that there is a significant correlation between the Φ_F parameter and the degree of branching. Thus, Φ_F turns out not to be a universal constant, but actually varies with the macromolecular topology.

For the evaluation of the influence parameters such as the degree of branching, molar mass, and functionality, a series of model polymers is required in which only one structural parameter is varied. Owing to the very broad molar mass and the superimposed branching distributions, a reliable elucidation of branching parameters is nearly impossible. Specific findings with natural and synthetic polymers led only to a complex and vague view of the scaling characteristics.^[4] Complementary results were obtained by computer simulations.^[5] We are in the position to analyze this behavior with hyperbranched (hb) structures and to extract particular information with regard to their highly branched character using a portfolio of different degrees of branching for fixed chemical structure, molar mass, and functionality. The interpretation of the molecular shape, density, or self-similarity can be determined by viscosity measurements and scattering methods.

The observed intrinsic viscosity is often expressed by a power-law behavior with an exponent of α_η , which includes scaling information. One possibility is the Kuhn–Mark–Houwink–Sakurada (KMHS) dependence of the intrinsic viscosity on the molar mass [Eq. (3)].

$$[\eta] = K_\eta M^{\alpha_\eta} \quad (3)$$

Typically, the value of the KMHS exponent is related to the shape and compactness of a polymer in a certain solvent. In numerous investigations, values of $0.3 < \alpha_\eta < 0.5$ were found for hb polymers.^[4a] Depending on the solvent quality, values of $0.5 < \alpha_\eta < 0.8$ were found for linear random coils. For hard spheres values close to zero are typical.

Substantial information on the size of the molecules can be obtained by scattering techniques. Static light scattering (SLS) gives the radius of gyration, R_g , and dynamic light scattering (DLS) gives access to the hydrodynamic radius, R_h . At sufficiently large $R_g > \lambda/20$ an angular dependence occurs and permits the determination of R_g . Unfortunately, the wavelength of the visible light is too long to allow the detection of sizes typical for hyperbranched macromolecules ($R_g < 10$ nm). Therefore, we use small-angle neutron scattering (SANS), which by working at very small scattering angles, covers wavelengths between 0.5 and 2 nm.^[6]

Similar to the KMHS relationship, the molar mass dependence of the gyration radius includes the evaluation of the scaling parameter, ν , in Equation (4).

$$R_g = KM^\nu \quad (4)$$

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The same relationship should be valid for the hydrodynamic radius, since in the ratio of R_g and R_h [Eq. (5)] the molar mass cancels out.

$$\rho \equiv \frac{R_g}{R_h} \quad (5)$$

Thus, ρ should remain constant^[7] but is also related to the segmental density in the polymer.^[8] Calculations predict that this value should be approximately 1.22 for hyperbranched polymers.^[4c] Values of $\rho=0.78$ and $\rho=1.78$ correspond to hard sphere and linear coil in a good solvent, respectively.^[4c,9]

Measurements of the molecular size in dilute solution additionally yields quantitative values for the degree of branching in long-chain branched polymers (that is, polymers with branches that are long chain), as calculated by Zimm and Stockmayer.^[10] These considerations are based on the apparent shrinking when a linear chain is transformed into a branched one of the same molar mass. This size reduction can be estimated by direct measurement of the radii of gyration R_g for the branched and linear chains leading to a molar mass dependent contraction factor g as defined by Equation (6).

$$g = \frac{R_{g,\text{branched}}^2}{R_{g,\text{linear}}^2} \Big|_M \quad (6)$$

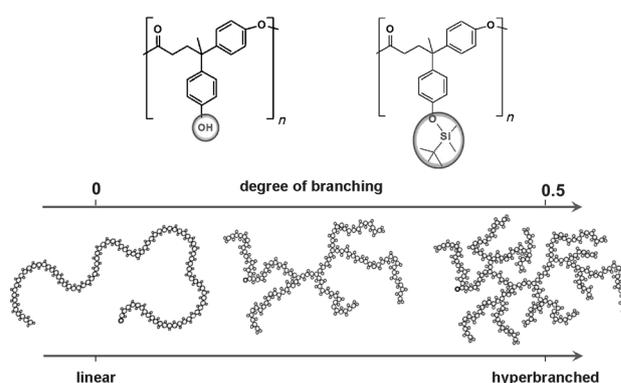
The contraction factor is a function of the number of branches n per monomer unit and depends on the functionality of the branch points. For monodisperse trifunctional branched fractions, Zimm and Stockmayer^[10] derived the g parameter as a function of branching points n and obtained Equation (7).

$$g = \left[\left(1 + \frac{n}{7}\right)^{1/2} + \frac{4n}{9\pi} \right]^{-1/2} \quad (7)$$

The intrinsic viscosity is a function of the size of the molecules, as described by the Flory–Fox equation [Eq. (2)], thus the size reduction can be also expressed by the ratio of the intrinsic viscosities of the branched and linear polymer [Eq. (8)].

$$g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}} \Big|_M \quad (8)$$

We performed SANS and dynamic light scattering to determine the global parameters of aliphatic–aromatic polyesters with degrees of branching from 0 to 50% (DB = 0 to 0.5 according to Frey et al.^[11]). We investigated two series of polymers, 1) with non-polar *tert*-butyldimethylsilyl groups and 2) with polar OH groups, to evaluate the influence of the functionality type on the scaling parameters ν and α_η . Our controlled synthesis path yields polymers with unique properties: the number of functional groups per monomer unit is unity. This number remains the same for all branching degrees.^[12] This goal was achieved by protecting one of the two B groups in an AB₂ monomer, and after polymerization the protecting groups were removed. In this way silyl-



Scheme 1. Variation of the branching degree from linear to hyperbranched structures for polyesters with different functional groups.

functionalized (SY) series and OH-functionalized series were available (Scheme 1).

The radii of gyration and the hydrodynamic radii of both series are listed in Table S1 of the Supporting Information and are plotted in Figure S1. Independent of the functionality type, R_g and R_h differ significantly from each other at low degrees of branching, but at high DB values ($\rightarrow 50\%$) R_g and R_h approach similar values. This effect stands in direct correlation to the segmental density of the polymers. It can be described by the structure-dependent ratio ρ [Eq. (5)], which is related to the segmental density of the molecule. We obtained values of ρ from 1.2 to 1.4 for the OH samples and 0.98 to 1.2 for the SY samples (Figure 1). The ρ value for the

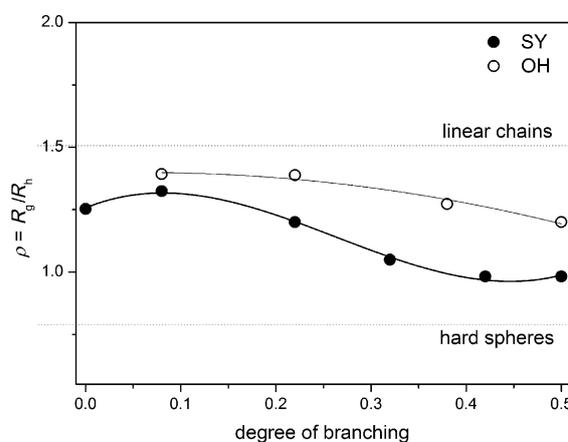


Figure 1. Dependence of the branching parameter ρ on the degree of branching for SY- and OH-terminated samples. The lines correspond to tentative fits to the measurement points.

linear polymers lies in the expected range for linear coils, whereas the hyperbranched OH-50 approaches the theoretically predicted $\rho=1.22$.^[4c] For SY-50 we obtain $\rho=0.98$, which corresponds to the experimental values observed for glycogen and amylopectin.^[8,13]

The aim of our work was to check the universality of the Flory–Fox equation [Eq. (2)] for molecules of branched topology. The Φ parameter could be calculated by Equation (2) using the intrinsic viscosity (Table S1) together with the radii of gyration. The results are plotted in Figure 2. The

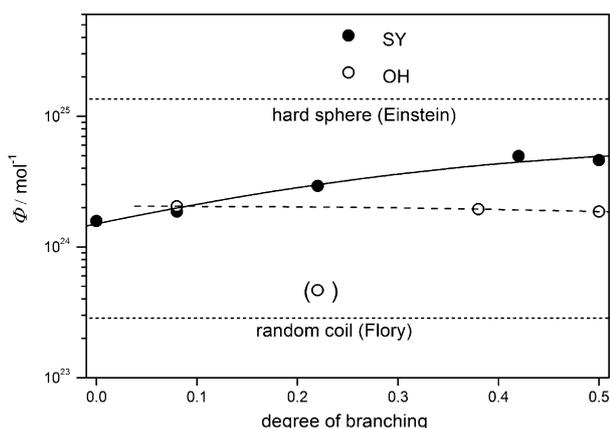


Figure 2. Dependence of the Flory–Fox parameter on the degree of branching for SY- and OH-terminated samples.

plot contains additionally the values of $\Phi_{\text{Flory}} = 2.86 \times 10^{23} \text{ mol}^{-1}$ for random coils^[14] of linear chains and $\Phi_{\text{Einstein}} = 13.57 \times 10^{24} \text{ mol}^{-1}$ for hard spheres.

For the hyperbranched OH samples nearly no variation with the DB was found but the values are greater by the factor of 7 than the Flory parameter for random coils. For the SY samples the Φ parameter clearly increases with the degree of branching. Even at DB = 0, a value six-times larger than that predicted by Flory was found for polystyrene in a good solvent.^[3] For both sample series a close correlation to the behavior of the apparent density $d_{\text{app}} = (3/4\pi)M/R_g^3$ is observed (Figure S5). The results for the OH end-groups are difficult to interpret but most likely the polar groups can undergo strong intramolecular interactions. Whatever the interpretation of the OH samples may be, the conclusion is that the Φ parameter is not a universal parameter but depends on the topology of the macromolecules.

The non-universality of the Φ parameter has consequences for another relationship, which was assumed to be universal for macromolecules. We continue our interpretation with the elucidation of the correlation of the contraction factors to the degree of branching, as described in Equations (6)–(8). Measurements of the intrinsic viscosity are much easier to perform than those of the radius of gyration. Therefore, it would be helpful to have a relationship, which allows us to calculate g from the g' factor. For the calculation of g from Equation (6), we used fractions from the linear SY-0 and the hyperbranched SY-50 polymers (see Supporting Information). For most of these fractions the molar mass was too low so that the R_g could not be accurately measured as a function of the molar mass. Therefore, we used the molar mass dependence of R_h and transformed it into R_g as outlined below. The fractions were characterized by dynamic light scattering. The molar masses and radii are listed in the Table S2. The R_h versus molar mass dependencies of both series, as well as the corresponding values of g are shown in Figure S2.

Stockmayer and Fixman^[15] noticed that with the assumption of universality for Φ a power-law correlation between g' and g should be observed since $[\eta]$ is related to R_g^3 and g to R_g^2

which leads to $g' \propto g^{3/2}$, a dependence which has never been found by experiments. Zimm and Kilb^[16] tried to solve the hydrodynamic behavior of branched samples to find the correlation between g' and g , but they had to make assumptions for the hydrodynamics, and found $g' \propto g^{1/2}$. These two values for the exponent 1.5 and 0.5, can be considered as the two possible limits in a range that would be realized by branched samples. This fact induced Kurata^[17] to assume the power law in Equation (9) with an exponent ε yet to be determined by experiment.

$$g' \propto g^\varepsilon \quad (9)$$

At that time star molecules with up to 12 arms were available. The experimental data with these star-macromolecules were found to be in the range around $\varepsilon \approx 0.6$.^[18] Some years later star molecules up to 128 arms became available. Roovers et al.^[19] carried out highly accurate measurements on g' and g and clearly demonstrated an increase of the exponent from fairly low values to $\varepsilon \approx 1$ when the number of arms was increased from 3 to 128. Thus, Stockmayer and Fixman conclude that the ratio $\Phi_{\text{branched}}/\Phi_{\text{linear}} \equiv \Phi^*$ in Equation (10) must be larger than 1.

$$g' = \frac{\Phi_{\text{branched}} R_{g,\text{branched}}^3}{\Phi_{\text{linear}} R_{g,\text{linear}}^3} = \Phi^* (g) g^{3/2} \quad (10)$$

This relationship includes the non-universality of Φ^* . Therefore we cannot expect ε to be a universal exponent, but ε could be constant, that is, independent of the molar mass, though depending on the degree of branching. To demonstrate this conjecture, the molar mass dependence of g and g' has to be determined. We investigated this by using two approaches:

1) The radius of gyration can be obtained from the measurement of the hydrodynamic radius, then multiplying these data by ρ , where ρ was determined from the samples measured by SANS (see Supporting Information). Together with the measured ρ values for SY-0 and SY-50 (shown in Table S1 and Figure S3) the molar mass dependence of g_ρ is obtained through Equation (11).

$$g_\rho \propto M^{-0.40} \quad (11)$$

2) In the second approach we estimated the number of branching points using the Zimm–Stockmayer Equation (7), where we used the correlation that the number n of branching points is proportional to the degree of branching. We then obtained Equation (12).

$$g_n \propto M_w^{-0.44} \quad (12)$$

The two estimations of g_ρ and g_n according to points (1) and (2) lead to somewhat different exponents but can be considered to lie within the experimental errors.

On the other hand, the contraction factors g' were calculated from the previously determined KMHS dependencies for SY-0 and SY-50,^[12] listed in Table S1 and shown in Figure S2. From the molar mass dependencies of the intrinsic

viscosity the molar mass dependence of g' is obtained as Equation (13).

$$g' \propto M_w^{-0.34} \quad (13)$$

We have to recall that both g and g' require the comparison of the radii and viscosity of branched and linear polymers of the same molecular mass. Thus it was necessary to use the molar mass dependencies, because it is not possible to prepare samples of exactly the same molecular mass. Note that the dependence of g' from the molar mass is -0.34 which is higher than the predicted exponent of -0.5 for g [see Eq. (7)].

Based on this information we can estimate the ε exponent by using the generalized Equation (10) and obtained for SY-50 Equation (14).

$$g' \propto g_n^{0.77} \quad (14)$$

We extended our calculations of ε to the series of polymers with branching degrees between 0 and 50%. The dependence on DB of the exponents from Equations (12) and (13) is shown in Figure S4. The dependence of the exponent ε on DB is shown in Figure 3.

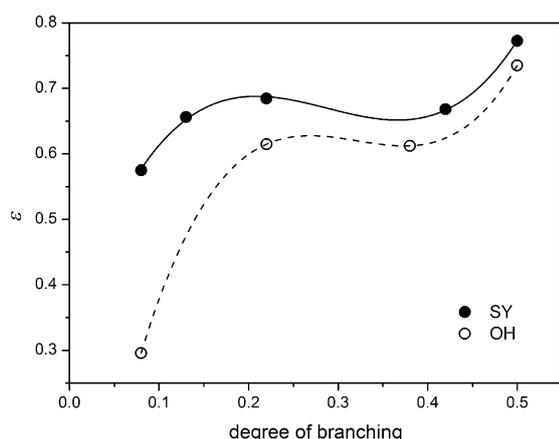


Figure 3. Dependence of ε [Eq. (9)] as a function of the degree of branching (DB) for SY- and OH-terminated samples. The lines are not fits but are to guide the eye.

Between DB 0.15 and 0.50 the ε exponent has only a small decrease with a decreasing degree of branching, and taking into account the experimental errors we could estimate $\langle \varepsilon \rangle = 0.72 \pm 0.05$. Below DB = 0.15 a large decrease towards $\varepsilon = 0$ takes place. The behavior of both series is similar but the OH exponent lies consistently below that of SY. Apparently, at large degrees of branching a certain universality of the ε exponents, that is, independence of the branching density, can be stated. However, this certainly does not hold for the less-branched samples.

To our knowledge this is the first visualization of ε as a function of the statistical branching degree. The question arises why does ε decrease and, in particular, what is the meaning of $\varepsilon = 0$? A look at Equation (10) makes it clear that the Φ^* parameter must also have a power-law correlation of

$\delta = \varepsilon - 1.5$ to the g parameter. In the limit of $\varepsilon \rightarrow 0$ we find $g' = g = 1$ and $[\eta] = \Phi_{\text{linear}} \frac{R_g^3}{M}$. This leads us to the conclusion that in every case at DB = 0, the ε exponent must become zero and the somewhat unexpected decrease of ε is a sensible finding. What remains is to find an explanation for why the OH data are consistently lower than those from the SY series. A indication is given by looking at $\Phi^*(g)$. If we assume a constant Φ_{linear} for linear chains this gives Equation (15) because $g \leq 1$.

$$\Phi^*(g) \propto \Phi_{\text{branched}} \propto 1 g^{(3/2-\varepsilon)} \quad (15)$$

The decrease of g , and thus, an increase of DB causes an increase of Φ_{branched} . This increase is quite substantial, as may be demonstrated by some experimental findings. Luca and Richards^[20] obtained $\delta = -1.22$, Kurata et al.^[18] and Weissmüller and Burchard^[21] $\delta = -0.9$, and in this study $\delta = -0.76$ and -0.73 for the OH and the SY samples at DB = 0.5. To recall, Zimm and Kilb predicted $\delta = -1$ and Stockmayer and Fixman $\delta = 0$. These data seem to suggest that the approximate hydrodynamic calculations by Zimm and Kilb are correct and probably describe the limit of very high branching densities.

The slight deviation of our results to the previous studies could be explained by the particularly low segmental mobility in the aliphatic–aromatic hyperbranched polymers.^[22]

In conclusion, an increase of the ε exponent corresponds to an increase of Φ_{branched} in the molar mass dependence of the intrinsic viscosity, caused by the branching density. Thus the main finding in our study is:

The Φ parameter is not a universal quantity but rather a function of the branching density.

Going back to the Zimm and Kilb theory it is the segmental density which perturbs the hydrodynamic flow and this segmental density is evidently controlled by the degree of branching. This fact influences the interpretation of size determination by common analytical techniques, for example, size exclusion chromatography. A number of investigations were focused on the validation and improvement of the universal calibration approach.^[23] Successful identification of the factors influencing this relationship could give a new possibility for calculating the radius of gyration even for branched polymers. Our result is of significant importance for describing common hyperbranched systems, in which the distribution of the molar mass is usually accompanied by a distribution in the branching degree. Therefore the development of multidimensional separation techniques has a high priority in the analysis of branched polymers. Recently, Radke et al.^[24] were successful in separating statistically branched polymers depending on the branching degree by using liquid chromatography under critical conditions. This innovative approach together with our results will in future enable a facilitated distinction of the effect of different structural parameters on the solution and material properties of hyperbranched polymers.

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