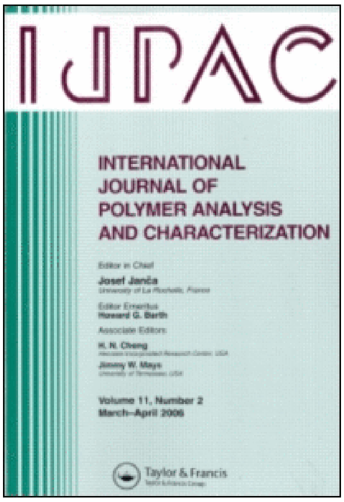

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Note on the Relation between the Parameters of the Mark-Houwink-Kuhn-Sakurada Equation

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Note on the Relation between the Parameters of the Mark-Houwink-Kuhn-Sakurada Equation

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The relation between the parameters K and a of the equation $[\eta] = KM^a$, *which has been empirically established by several authors, is discussed. Equations describing this relation are derived based on the two-parameter theory of the intrinsic viscosity for flexible chain polymers (where* $a < 0.8$*) and on the worm-like cylinder model for stiff chains (*$a > 0.8$*). The correspondence of calculated and empirical results is good.*

Keywords: Equation $[\eta] = KM^a$; Parameters K and a; Interpretation

The dependence of the intrinsic viscosity $[\eta]$ on the molecular weight of polymers is currently described by the Mark-Houwink-Kuhn-Sakurada (MHKS) equation:

$$[\eta] = K.M^a \tag{1}$$

where the parameters K and a depend on the polymer-solvent system. They are estimated from the intercept and the slope of straight line fitting the bi-logarithmic plot of $[\eta]$ versus M:

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$$\ln[\eta] = \ln K + a \ln M \tag{1a}$$

In this approximation the quotient

$$a = d\ln[\eta]/d\ln M \tag{2}$$

is constant. Some authors[1–3] have established a simple relation between these parameters for a given polymer in various solvents. Based on a large body of experimental data for polymers referred to as flexible (with $0.5 < a < 0.8$), Rai and Rosen[4] have described this relation by the empirical equations

$$\log K = ma + c \tag{3}$$

and

$$\log(K/K_0) = m(a - 1/2) \tag{4}$$

where m, c, and K_0 are the parameters specific to the polymer. The m values for polymers examined by Rai and Rosen[4] oscillate around -3.94 (within 7%). Some time ago, Millich et al.[5] found than an equation similar to Equation (3) with $m = -4.64$ and $c = 0.55$ holds for stiffchain polymers differing in chemical structure and chain conformation ($0.8 < a < 1.8$).

To interpret the relation between K and a for flexible chains, Boyer and Simha[6] and, recently, Simha[7] have used theories of the intrinsic viscosity that attribute the solvent dependence of the MHKS parameters to the strength of the intramolecular hydrodynamic interaction. Kamide and Kataoka[8] based their interpretation on a semi-empirical theory that ascribes the variation to the expansion of chain dimensions by the excluded-volume effect. No attempt has been made so far to explain Equation (3) for stiff-chain polymers. As will be shown in this note Equation (3) can be rationalized for both types of polymers on the basis of recent theories of the intrinsic viscosity.

FLEXIBLE POLYMER CHAINS IN NON-DRAINING REGIME

The starting point of the discussion is the well-known Fox-Flory equation[9] for the intrinsic viscosity of random coils in the non-draining regime:

$$[\eta] = K_0 M^{1/2} \alpha_\eta^3 \tag{5}$$

The K_0 parameter is related to ratio $(\langle R^2\rangle 0/M)_\infty$ of the mean-square end-to-end distance $\langle R^2\rangle_0$ and the molecular weight of random coils unperturbed by the excluded-volume effect by

$$K_0 = \Phi_{0,\infty}\left(\langle R^2\rangle_0/M\right)_\infty^{3/2} \tag{6}$$

where $\Phi_{0,\infty}$ is the Flory viscosity constant in the non-draining regime, and the viscosity expansion factor α_η^3 is a function of the excluded-volume variable z defined by

$$k = z/M^{1/2} = 0.346\Phi_{0,\infty}(B/K_0) \tag{7}$$

A variety of functions $\alpha_\eta^3(z)$ have been advanced, some of them being a semi-empirical modification of theoretical results. Actually, the most consistent approach to the problem of the excluded volume effect on the intrinsic viscosity is due to Barrett[11]. Hence, the formula

$$\alpha_\eta^3 = \left(1 + C_1 z + C_2 z^2\right)^{0.3} \tag{8}$$

(with $C_1 = 3.8$ and $C_2 = 1.9$) resulting from his treatment appears to be suitable for the purpose of this article.

Differentiating Equation (5) with respect to the molecular weight and Equation (8) with respect to z leads to

$$d\ln[\eta]/d\ln M = 1/2 + d\ln\alpha_\eta^3/d\ln M \tag{9}$$

$$d\ln\alpha_\eta^3/d\ln z = 0.3\left(C_1 z + 2C_2 z^2\right)/\left(1 + C_1 z + C_2^2\right) \tag{10}$$

Combining Equations (1a), (2), (9), (5), and (10) we have

$$a = 1/2 + d\ln\alpha_\eta^3/d\ln M \tag{11}$$

and

$$\ln(K/K_0) = \ln\alpha_\eta^3 - 0.15\left(C_1 z + 2C_2 z^2\right)\left(1 + C_1 z + C_2 z^2\right)^{-1}\ln M \tag{12}$$

As follows from Equations (9) and (11) the quotient $d\ln\alpha_\eta^3/d\ln M$ is a function of the molecular weight, and the same applies for the ratio K/K_0 (see Equation (12)) and the MHKS parameters K and a.

Equations (10)–(12) will be used to calculate the dependence of K/K_0 versus a. Figure 1 presents plots of log (K/K_0) versus a computed for the case that the polymer-solvent interaction parameter B is kept constant and the z variable varies with the molecular weight according to Equation (7). To construct these curves we set the k parameter (see Equation (7))

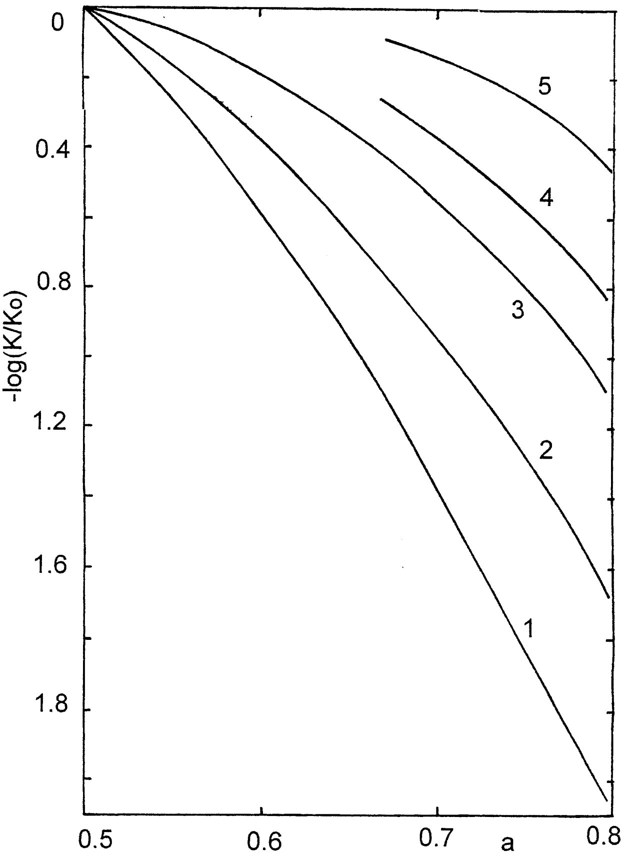

FIGURE 1 Theoretical relation between the MHKS parameters; curves 1 to 5 calculated using Equations (10) to (12) for constant k values (10^{-4}, 10^{-3}, 10^{-2}, 0.4, and 0.1) and varying molecular weights.

equal to 10^{-4}, 10^{-3}, 10^{-2}, 4×10^{-1}, and 10^{-1} as characteristic of the polymer-solvent system, and calculated the exponent a with Equation (11) and K/K_0 using Equation (12), for molecular weights in the range from 10^2 to 10^{12}. The figure shows that the dependence of K/K_0 versus a is the weaker and the ratio K/K_0 at $a \rightarrow 0.8$ is the higher the k parameter. The theory predicts that the a and K values should depend on the molecular weight. In practice, this dependence can hardly be detected due mainly to limited ranges of molecular weights used in most experimental studies.

The plots in Figure 2 are equivalent to the plots in Rai and Rosen[4] of data for a given polymer in various solvents differing in the interaction parameter. The curves were obtained from dependences similar to those in Figure 1 by interpolation for molecular weights $M = 10^4$, 1.5×10^5, and 10^6. While the curves for the two highest molecular weights considered are close to one another, the curve for $M = 10^4$ is distinctly different. All curves can be approximated by straight lines for $a < 0.67$, whereupon they flatten and pass through a minimum at $0.73 < a_{\min} < 0.76$. The dependence of K versus a calculated with Equation (4) and the mean value ($m = -3.94$) reported by Rai and Rosen[4] is drawn by dashed straight line. The correspondence with the results of this article is good.

The minima and sharp increase of the curves at $a > a_{\min}$ are worth discussion. The $a_{\min}$ values are the higher and the minima are the deeper the higher the molecular weight. Bi-logarithmic plot of α_η^3 versus M in Figure 3 can help to explain this behavior. We first consider the section of curves between $M = 10^4$ and 10^6, i.e., in the region of practical interest. Dotted lines represent linear approximation to calculated curves in this

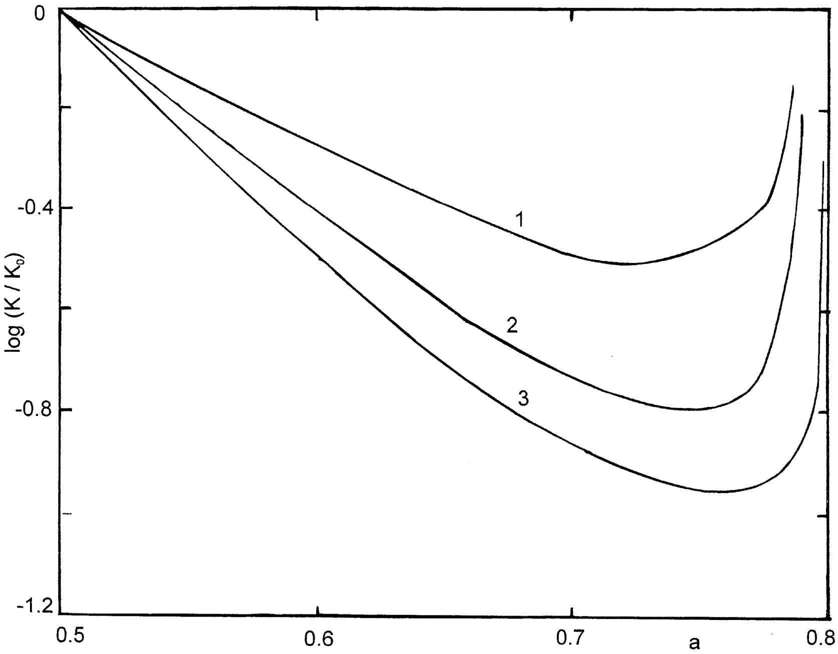

FIGURE 2 Theoretical relation between the MHKS parameters; curves 1 to 3 calculated for a fixed molecular weight (10^4, 1.6×10^5, 10^6) and varying interaction characteristic k. Details in text.

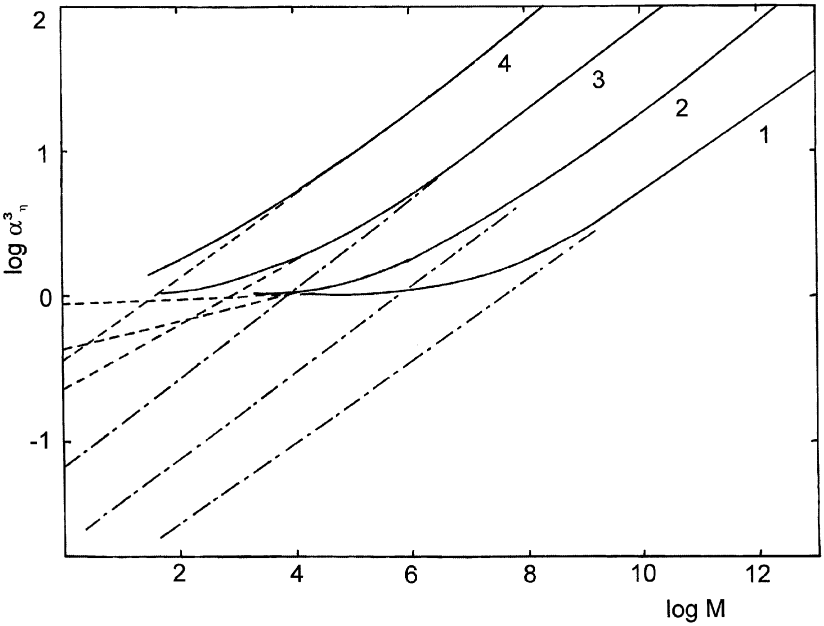

FIGURE 3 Molecular weight dependence of the viscosity expansion factor α_η^3; full curves 1 to 4 calculated using Equations (8) and (7) for $k = 10^{-4}$, 10^{-3}, 10^{-2}, 10^{-1}; short dashed lines schematically represent linear fits to curves at $10^4 < M < 10^6$; dashed dotted lines represent linear fits to asymptotic parts of curves.

range, and their intercepts (at $\log M = 0$) are equal to $\log(K/K_0)$. These decrease with increasing k at $k < 10^{-2}$ only. At $k = 0.1$ the intercept is higher than that for 10^{-2} and is almost equal to that for $k = 10^{-3}$. This is consistent with the shape of the curves in Figure 2.

Let us consider the ascending branches of curves in Figure 2. In this region the a values approach to $a = 0.8$ predicted by theory for very good solvents and very high molecular weights. The k values are of the order of 10^{-1}, and the molecular weights would be higher than the highest molecular weight found with flexible chain polymers ($M \cong 6 \times 10^7$ for polystyrene[10]). The k values correspond to extremely good solvent systems where, as can be seen in Figure 3, the chain expansion due to the excluded-volume effect would be noticeable already at molecular weights of the order of hundreds. No solvents of such power have been known so far. Moreover, the chain stiffness, which is not taken into account in our calculations, would probably be dominant in this range.

By extrapolating the asymptotic parts of the curves in Figure 3 to log $M = 0$, the values of $\log(K/K_0)$ corresponding to this region are estimated. They increase with increasing k values, i.e., with increasing strength of the polymer-solvent interaction. In principle, values close to zero could be obtained with $k > 0.1$.

Curves similar to those in Figure 2 have been reported by Kamide and Kataoka[8] and by Colby[12]. The starting poinZt of the former authors was similar to that used in this article, i.e., the two-parameter theory. The latter author applied the scaling approach to the intrinsic viscosity.

In Figure 4 we have plotted data for polyolefins and polydienes[13–15], poly(methyl methacrylate) (PMMA)[3,15,16], polystyrene (PS)[3], poly (vinyl

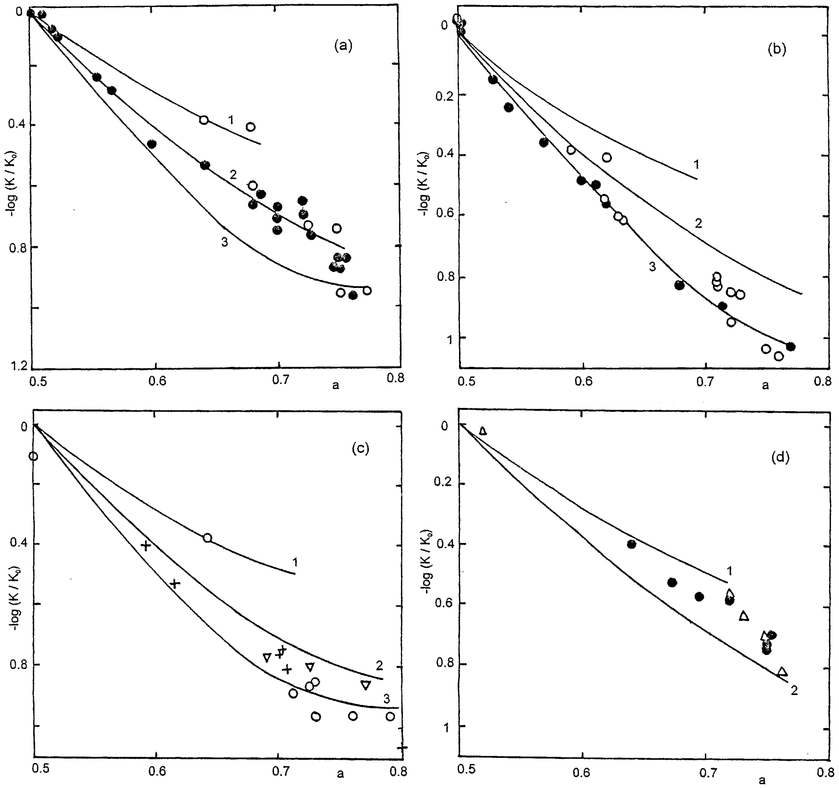

FIGURE 4 Relation of experimental values of the MHKS parameters for polymers in different solvents; (a) polyolefins ○ and polydienes ●[13–15], (b) polystyrene[3] in single ○ and mixed ● solvents, (c) poly(methyl methacrylate) ○[3], ▽[20], + [17],(d) poly(vinyl chloride) ●[17,18], △ poly(ε-caprolactame)[19]. Curves 1 to 3 calculated for $M = 10^4$, 1.6×10^5, and 10^6.

chloride) (PVC)[17,18] and poly (ε-caprolactame) (PCL)[19], making use of values of a, K, and K_0 given in the respective articles or calculated from $[\eta]$ and M listed therein. Theoretical curves in these figures correspond to a fixed molecular weight ($M = 10^4$, 1.6×10^5, and 10^6), i.e., to one point in the bi-logarithmic plot of $[\eta]$ versus M. Contrary to this, experimental K and a values correspond to a section of such plot, in other words, to a certain interval of molecular weights. In order to make possible a comparison of calculated and experimental data, we characterize these intervals by the geometric mean M_g of the highest and lowest molecular weights used in the respective experimental studies, i.e., $M_g \times 10^4 \cong 18$ for PMMA and PS, 10 for polyolefins and polydienes, 5 for PVC, and 6.3 for PCL. It is seen that experimental plots in these figures are well explained by the results of calculations carried out in this article if differences in ranges of molecular weights are taken into account.

With respect to this finding, we did not adopt the more sophisticated quasi-two-parameter theory although, as has been shown in recent studies by Yamakawa's school (see Fujii et al.[20]), it significantly improves the correspondence of experimental and theoretical values of α_η^3, particularly at lower molecular weights. This scheme takes into account the impact of chain stiffness on the onset of the excluded-volume effect.

When constructing Figure 4 we did not use the MHKS parameters estimated from the correlation of the intrinsic viscosity with the number average molecular weight because of its high sensitivity on polymolecularity. We have also excluded data for polymers whose chains may be branched (e.g., polyethylene, polyacrylates, poly(vinyl acetate), etc.) or for aggregating systems. In the former case the degree of branching usually increases with increasing molecular weight, in the latter, incomplete removal of super molecular particles before light scattering increases the molecular weights. In both cases, the bi-logarithmic plots of $[\eta]$ versus M are deformed, yielding lower a and higher K values.

STIFF-CHAIN POLYMERS

As the MHKS exponent for stiff-chain polymers is typically higher than 0.8, the interdependence of the K and a values cannot be interpreted in the manner outlined in the first part. In this part we are concerned with this problem for stiff chains under a simplifying, although realistic, condition that the excluded-volume effect on the chain dimensions and intrinsic viscosity can be neglected.

The starting point is the result of the Yamakawa-Fujii theory[21]

$$[\eta]_0 = K_0 M^{1/2} F_1(L_r, d_r) \tag{13}$$

where K_0 is given by Equation (6), and d_r is the reduced cross-sectional diameter of the worm-like cylinder model expressed in multiples of the Kuhn statistical segment length l_k. This is given by

$$l_k = \left(\langle R^2\rangle_0/M\right)_\infty M_L \tag{14}$$

where M_L is the "shift" factor, which is usually set equal to the molecular weight per unit contour length. It follows from the theory that the quotient $v = d\ln[\eta]/d\ln M$ and, consequently, the exponent a in the MHKS equation, is a function of the molecular weight:

$$a = 1/2 + v \tag{15}$$

By combining Equations (1), (13), and (15) we obtain

$$\log(K/K_0) = \log F_1 - v\log M \tag{16}$$

or, in a form more convenient for calculations,

$$\log(K/K_0) = \log F - v\log L_r - v\ln M_K \tag{17}$$

where M_K is the molecular weight of the Kuhn segment ($M_K = M/L_r$).

The function F_1[21] can be well approximated[22,23] by

$$F_1 = (B_0 + A_0/L_r)^{-3} \tag{18}$$

where A_0 and B_0 are functions of d_r[23]. It should be remembered that Equation (18) works well at L_r values higher than L_r^* values (of order of unity)[23]. Using the A_0 and B_0 values for see Bohdanecký $d_r = 0.001, 0.01, 0.1, 0.2$, and 0.4 we have first computed F_1 and v for $L_r > L_r^*$ and then the values of K/K_0 for three segment molecular weights M_K ($10^4, 10^5$, and 10^6). The results are presented in Figure 5.

As follows from theory[23], calculated curves are limited to $a \geq 0.9$. The plots show that the K values for very thin chains ($d_r \cong 0.001$) can be lower than K_0 by as much as eight orders of magnitude. The effect of chain thickness is weak for $d_r < 0.01$ but very strong for higher d_r values. At $d_r \cong 0.4$ the ratio K/K_0 is about unity, irrespective of the chain length. The effect of the segment molecular weight is remarkable: the higher the molecular weight M_L, the higher is the negative slope of the plot.

The straight dotted line in Figure 5 is a schematic representation of Equation (4) with Millich's value $m = -4.64$[5]. It is nearly parallel to theoretical curves for $0.01 < d_r < 0.1$ and $10^4 < M_K < 10^5$. The values of these characteristics are not available for all polymers mentioned in Millich et al.[5], nevertheless, it is encouraging that the values ($0.02 < d_r < 0.034, 4.5 < M_K \times 10^4 < 44$)[23] for one of them (cellulose trinitrate) are in this range. The same applies for two polypeptides (poly

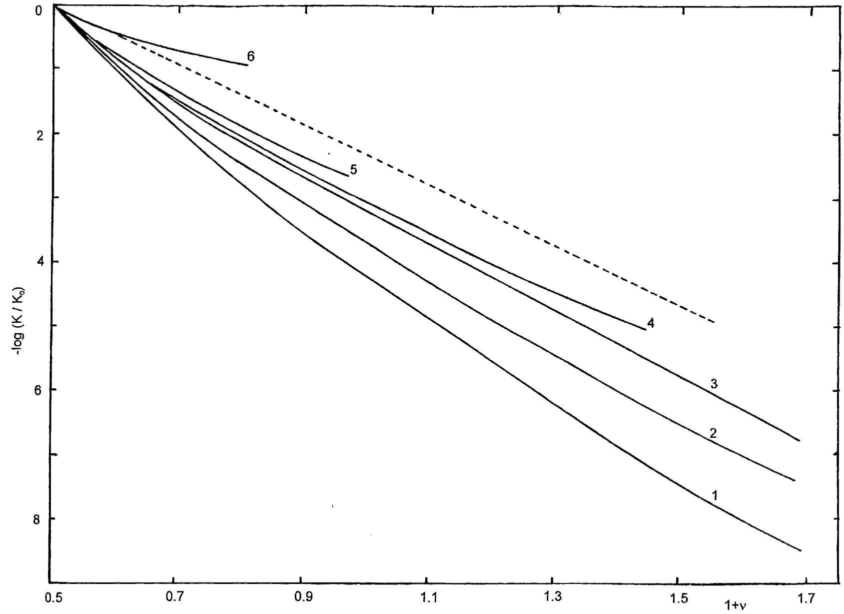

FIGURE 5 Relation between the MHKS parameters of stiff chain polymers; curves 1 to 6 calculated for (M_K, d_r): (10^6, 10^{-3}), (10^5, 10^{-3}), (10^4, 10^{-3}), (10^4, 10^{-2}), (10^4, 0.1), (10^4, 0.2). Dashed line calculated using Equation (3) with $m = -4.64$ and $c = 0.55$[5]. Details in text.

(ε-carbobenzoxy-L-lysine) and poly (γ-ethyl-L-glutamate)[23] which are similar in structure to polypeptides studied by Millich et al.[5] ($d_r \cong 0.015$, $M_K \cong 10^5$).

We can conclude that the empirical relation between the MHKS parameters for stiff chains as presented in Millich et al.[5], can theoretically be explained. Nevertheless, it should be borne in mind that the dependence would be milder with "thicker" polymer chains ($d_r > 0.1$).

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