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A Novel Approach to Theories of Polymer Coils in Good Solvents

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ABSTRACT

A new theory is proposed involving a short-range interaction parameter, N_0 , which allows for finite chain effects. The parameter z , which was originally suggested by Yamakawa, is redefined to make it applicable to finite chains. The dependence of intrinsic viscosity on molecular mass as predicted by most of the acknowledged theories of polymer solution seem to be incompatible with the Mark-Houwink-Sakurada relation. This makes the evaluation of interaction parameters from viscosity data difficult. Therefore, an attempt is made here to show that these theories contain some basic assumptions (and/or mathematical simplifications) which may lead to erroneous conclusions.

INTRODUCTION

The intrinsic viscosity, $[\eta]$, of a polymer solution depends both on hydrodynamic and thermodynamic factors. Traditionally, a polymer

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molecule may be characterized by an equivalent hydrodynamic radius, which depends on the size, shape, and distribution of mass within the polymer coil as well as its hydrodynamic permeability. If, for a class of systems, the coils are hydrodynamically impermeable, and the shape and distribution of mass are the same, then the ratio between the hydrodynamic radius and the end-to-end distance, r , is the same for all members of that class. Simple analysis then shows that

$$[\eta] = \phi r^3 M, \quad (1)$$

where M is the molecular mass of the polymer and ϕ is a parameter which depends on the hydrodynamic factors (except r) and is a constant for the class. The linear polymers dissolved in pseudo-ideal theta-solvents form such a class. In this case, the parameter ϕ becomes $\phi_0 = 2.87 \times 10^{23}$ ($[\eta]$ in L/kg), and r has an "unperturbed" value r_0 . Equation (1) may now be transformed into

$$[\eta]_{\theta} = \phi_0 (r_0^2/M)^{3/2} M^{1/2} = K_{\theta} M^{1/2}, \quad (2)$$

where $K_{\theta} = \phi_0 (r_0^2/M)^{3/2}$. The parameter of unperturbed dimensions, r_0^2/M , and the constant, K_{θ} , depend on the chemical structure and stiffness of the macromolecules in addition to the temperature and the nature of the solvent. Experimentally, it has been shown [1, 2] that the ratio $[\eta]_{\theta}/M^{1/2}$ is very nearly independent of molecular mass down to very low molecular masses. In good solvents the polymer-polymer contacts are favored less than in the case of theta-solvents. Consequently, the end-to-end distance, r , is larger than r_0 , and thus $\alpha_R \equiv r/r_0$ is greater than unity. The distribution of polymer segment densities and parameter ϕ may also differ. Customarily, the parameters for a pseudo-ideal coil are factored out from Eq. (1), which is written in a form similar to Eq. (2) as

$$\begin{aligned} [\eta] &= \phi_0 (r_0^2/M)^{3/2} M^{1/2} (\phi/\phi_0) (r/r_0)^3, \\ &\equiv K_{\theta} M^{1/2} (\phi/\phi_0) \alpha_R^3, \\ &\equiv K_{\theta} M^{1/2} \alpha_{\eta}^3, \\ &= [\eta]_{\theta} \alpha_{\eta}^3, \end{aligned} \quad (3)$$

where the viscosity expansion coefficient $\alpha_{\eta}^3 \equiv (\phi/\phi_0)(r/r_0)^3$.

Experimentally [3], most of the polymer-solvent systems obey the empirical two-parameter Mark-Houwink-Sakurada (MHS) relation

$$[\eta] = KM^{\underline{a}}, \quad (4)$$

which may be rearranged to

$$\begin{aligned} [\eta] &= K_{\theta} M^{1/2} (M/M_0)^{\underline{a} - (1/2)} \\ &= [\eta]_{\theta} \alpha_{\eta}^3, \end{aligned} \quad (5)$$

where the definition of the characteristic mass, M_0 , is obvious from a comparison of Eqs. (4) and (5). Most experimental data follow Eq. (4) quite closely in the region of molecular masses that are at least several times higher than M_0 ($M_0 \approx 5000$ g/mol for polystyrene and poly(methyl methacrylate)). In a previous study [1] it has been shown that the parameter K_{θ} can be calculated from the values of K and \underline{a} by using the assumption that the characteristic section of a macromolecule with mass M_0 always contains the same number of statistical segments. If the validity of Eq. (4) is accepted, then the exponent \underline{a} becomes a single parameter characterizing the particular polymer-solvent system; it increases with the thermodynamic quality of the solvent. However, the physical significance of the parameter \underline{a} is not obvious.

THEORETICAL

Most theories of polymer solutions model the polymer coil as a string of connected statistical segments. In the reference "unperturbed" state, the segment positions correspond to a random walk problem. One group of theories [2] describes the coil by means of the distribution function of all intersegmental distances. The difference between the real and the reference distribution function is treated as a perturbation, which is characterized by the binary cluster integral β . Another group of theories [4] treats the coil as a cloud of unconnected segments (the smoothed segment density model) which are subject to osmotic forces and are characterized by the familiar Flory-Huggins parameter χ .

The exact statistical analysis of the segment model is a formidable mathematical problem, and all the standard theories employ some simplifying assumptions. In this paper an attempt will be made to show that some of these assumptions may influence the final results significantly. It can be shown that the distribution function of the

intersegmental distances in the random-walk problem is almost indistinguishable from the Gaussian distribution when the two segments are separated by a sufficiently large number of links [5]; ten links already give an excellent fit. Moreover, the same Gaussian distribution is obtained when the single segment-segment link itself is replaced by a Gaussian distribution of distances. The introduction of the Gaussian distributions significantly simplifies the mathematical analysis. Nevertheless, it represents a rather poor approximation for segments which are separated by only one or a very few links.

In the real chains, two problems arise: (1) two segments cannot overlap creating the excluded volume and (2) intersegmental contacts may be favored by a Boltzmann factor related to interaction energies. These effects are formally taken into account by introduction of a potential of mean force and the binary cluster integral, β , which represent the balance of the steric and interaction factors. For a special case $\beta = 0$, the probability of finding a segment in close vicinity of another segment is the same as if these real chain effects were absent; the coil is believed to behave in a Gaussian fashion. In a general case $\beta \neq 0$, the perturbation of the Gaussian coil is calculated as a function of β and of the number of links N .

In a standard approach originally due to Fixman [6], the perturbation of the end-to-end distance is calculated as a sum of terms which are related to single or multiple contacts within a coil. Each contact is characterized by the same value of β . The probability of two segments making a contact is derived from the Gaussian statistics of intersegmental distances. The results are written as

$$\alpha_R^2 = 1 + C_1 z - C_2 z^2 + C_3 z^3 - \dots, \quad (6)$$

$$z = (3/2\pi b^2)^{3/2} \beta N^{1/2}, \quad (7)$$

$$C_1 = N^{-3/2} \sum_{k=0}^N \sum_{l=k+1}^N (1-k)^{-1/2}, \quad (8)$$

where b is the mean square length of a Gaussian link between adjacent segments and $(1-k)$ is the number of links between two interacting segments. The standard analysis then calls for a conversion of the sums to integrals and their evaluation in the limit of very large N . After evaluation [2] of the constants C_i , Eq. (6) can be written as

$$\alpha_R^2 = 1 + (4/3)z - 2.07z^2 + 6.459z^3 - \dots. \quad (9)$$

The expansion factor for intrinsic viscosity, α_η^3 , was calculated by Yamakawa and Tanaka [7]. Their calculations were very involved,

and only the linear term was evaluated numerically as

$$\alpha_{\eta}^3 = 1 + 1.06z - \dots \quad (10)$$

According to this treatment, the expansion factors α_R and α_{η} are unique functions of the parameter z . This result is incompatible with the expression for α_{η}^3 derived from the MHS relation, Eq. (5):

(1) The MHS relation cannot be expanded into a power series of z , i.e., in powers of $M^{1/2}$. (2) The dependences of α_{η}^3 on $M^{1/2}$ for different solvents with different exponents a cannot be reduced to a single master curve. Therefore, further analysis of the assumptions underlying the standard perturbation treatment and the mathematical simplifications involved is indicated.

The evaluation of the double sum in Eq. (8) as a limit of an integral is satisfactory only for values of N that are much larger than values ordinarily of interest. We have transformed Eq. (8) into an equivalent equation, namely,

$$C_1 = N^{-3/2} \sum_{j=1}^N (N-j)j^{-1/2}, \quad (11)$$

which was then evaluated by a computer as a function of N . It was found that C_1 can be represented to a very good approximation by the relation

$$C_1 = (4/3)[1 - (N_0/N)^{1/2}], \quad (12)$$

where $N_0 = 1.2$. Inspection of the sum in Eq. (8) shows that the contacts between the adjacent and/or close segments contribute heavily to the sum for all values of N which are of interest.

Immediately the question arises: Is the contribution of these contacts evaluated properly? The Gaussian model assumes that the adjacent segments are frequently in contact, while the random-walk model (with steps of constant length b) implies that they are never in contact. Similar discrepancies exist even for close nonadjacent segments. The probability of contact between them may be severely reduced by steric constraints. This behavior can be formally taken into account by assigning to adjacent and close segment pairs a smaller (absolute) value of β or, for greater simplicity, a zero value. The sum in Eq. (11) was evaluated by assigning $\beta = 0$ to contacts with the first j_0 neighbor segments. The sum is again approximated by Eq. (12).

TABLE 1. Dependence of Parameter N_0 on the Number of Neighboring Segments for which Contacts Are Neglected

j_0	N_0
0	1.20
1	3.40
2	5.63
3	7.87
4	10.10

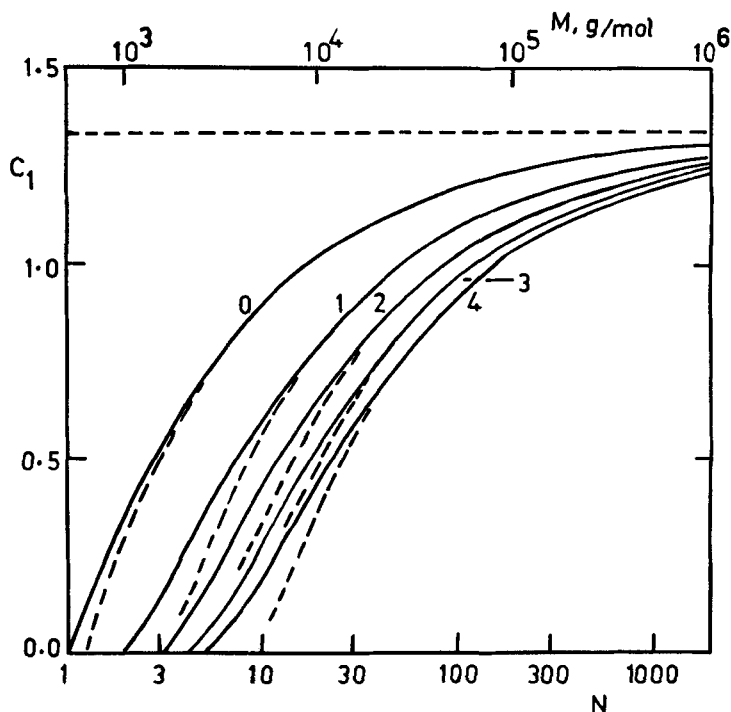


FIG. 1. Dependence of the factor C_1 on the number of segments N for several values of j_0 . Full lines represent the exact values of the sum in Eq. (11); broken lines represent Eq. (12). The horizontal broken line is the limiting value for very large N . The upper scale represents molecular masses, M (assuming a segment molecular mass of 500 g/mol).

The value of N_0 as a function of j_0 is given in Table 1, and C_1 is plotted as a function of N for several values of j_0 in Fig. 1. The correction term $(N_0/N)^{1/2}$ is by no means negligible: for $N = 200$, i.e., for a typical polymer, with a segmental molecular mass of 500 g/mol and a molecular mass of 100 kg/mol, it represents 8% of the value of C_1 if no contacts are neglected and 22% if four neighbors are neglected.

Substitution of Eqs. (7) and (12) into Eq. (6) yields

$$\alpha_R^2 = 1 + (4/3)(3/2\pi b^2)^{3/2} \beta(N^{1/2} - N_0^{1/2}) - \dots \quad (13)$$

Equation (13) impelled us to redefine the parameter z as

$$z = (3/2\pi b^2)^{3/2} \beta(N^{1/2} - N_0^{1/2}), \quad (14)$$

where the parameter N_0 characterizes short-range interactions.

With the new definition of z , Eq. (9) is recovered at least up to the linear term. We believe that use of the redefined parameter z is similarly justified in Eq. (10).

The expansion factor α_η^3 from Eq. (5) may be expanded into a similar series:

$$\begin{aligned} \alpha_\eta^3 &= (M/M_0)^{\underline{a}-(1/2)} \\ &= [1 + (M^{1/2} - M_0^{1/2})/M_0^{1/2}]^{2\underline{a}-1} \\ &\approx 1 + (2\underline{a} - 1)(M^{1/2} - M_0^{1/2})/M_0^{1/2} - (2\underline{a} - 1)(1 - \underline{a}) \\ &\quad (M^{1/2} - M_0^{1/2})^2/M_0 + \dots \end{aligned} \quad (15)$$

Realizing that $M/M_0 = N/N_0$, we may compare the linear terms in Eq. (15) with the combined Eqs. (10) and (14) to obtain

$$1.06\beta(3/2\pi b^2)^{3/2} = (2\underline{a} - 1)/N_0^{1/2}. \quad (16)$$

This treatment shows that the parameter of short-range interaction N_0 , which was originally introduced by the phenomenological analysis of the MHS relations in several solvents, fits quite naturally into the structure of the perturbation theory of polymer coils. The experimental value [3] of $N_0 = 9$ corresponds to an effective j_0 equal

to about 3.5. The modified theory is now compatible with the MHS relation, at least in the region of small expansion.

The treatment described above (both in its original and presently modified form) leads to the series in Eqs. (9) and (10), which converge very slowly. The mathematical complexity in the calculations of higher coefficients increases rapidly. Consequently, the series is useful, at best, for values of $\alpha_R^2 \leq 1.2$, i.e., only in the closest vicinity of the pseudo-ideal theta conditions. For the larger expansions of the polymer coil, a number of approximate theories has been proposed [2]. Their predictions differ greatly, but they have one factor in common: They predict the existence of a master curve of α_R^2 as a function of the z coordinate. This is again in contradiction to the MHS relation. It is possible that some of the theories, when modified by the introduction of the redefined z parameter, may describe the experimental data quite satisfactorily. In the meantime, however, we feel that none of them are reliable enough for a meaningful analysis of the experimental data.

The theories, including that of Flory and Fox [8], use the smoothed segment density model to calculate the expansion factor from the condition that the contribution of a single coil to the free energy of the system be minimum. The free energy is calculated as a sum of an elastic (entropic) term and a contact term. The entropy term is based on the statistics of the Gaussian coil, while the contact term is evaluated for a cloud of unconnected segments. The density of segments is taken to be the average density over all configurations, i.e., to an appropriate Gaussian function with spherical symmetry. The contribution of each volume element within the coil to the total contact term is calculated by assuming the validity of the Flory-Huggins theory for these volume elements. In this treatment, there is no difference between various types of expansion factors; the symbol α is used for all of them. The result of Flory and Fox [8] is

$$\alpha^5 - \alpha^3 = 2C_M(1 - \chi)M^{1/2}, \quad (17)$$

where C_M is a geometrical factor depending only on the unperturbed dimensions of the polymer, (r_0^2/M) , and on the molar volume of solvent. The right-hand side of Eq. (17) may be shown to be proportional to the parameter z : a single master curve is again expected for all polymer good-solvent systems. Moreover, the dependence of $\log[\eta]$ on $\log M$ is expected to be curved, with the limiting slope equal to 0.8 for a polymer of infinite molecular mass in good solvents. Consequently, this model is also incompatible with the MHS relation.

The smoothed density model predicts that, within a single coil, the number of polymer-polymer contacts per segment decreases with increasing molecular mass ($\sim M^{-1/2}$), i.e., the probability that any

given segment is in contact with other segments is less for polymers with high molecular mass than for those with low ones. This is in contrast with the more sophisticated chain model; as we have seen above, the probability of a segment making a contact is the sum of probabilities of contacts with the first, second, third, etc. neighbors. In the Gaussian (or pseudo-ideal) case, the segment of a macromolecule has the same probability of being in contact with its not-too-far neighbors as has the segment of a short molecule. Furthermore, it has a chance of being in contact with some distant segment. Of course, there are no distant segments in short molecules. Thus, the number of contacts per segment probably increases with increasing molecular mass. Consequently, the smoothed density model seriously distorts the dependence of the contact term and of the expansion factor on molecular mass.

There is also a difficulty with the value of the parameter χ . The treatment of Orofino and Flory [9] takes into account a possible dependence of χ on the concentration of the polymer. However, it is implicitly assumed that χ is independent of molecular mass. As χ is found experimentally to be strongly dependent on M , it is not obvious how to select a value of χ applicable to the smoothed density model.

CONCLUSIONS

The standard perturbation theory of a polymer coil evaluates the probability of a segment-segment contact within a coil by using an expression which is extrapolated to an infinite number of segments. By this procedure, a correction term $(N_0/N)^{1/2}$ is neglected which is significant for all molecular masses ordinarily of interest. Its omission distorts the predicted dependence of the expansion factor on molecular mass.

The Gaussian model predicts an unrealistically high frequency of contacts between segments. A modification of the model of the coil is proposed in which the contacts of a segment with j_0 (up to 3 and 4) neighboring segments are not taken into account. Such a modification results in an increase in the N_0 value in the correction term.

In view of the neglect of such a significant term, it is not surprising that the dependence of the expansion factor on molecular mass predicted by the standard perturbation treatment (Eqs. 6, 7, and 10) is incompatible with the dependence described by the MHS relation, Eq. (5). It is, therefore, proposed that a partial remedy may be achieved by redefining the parameter z (Eq. 14). This redefinition implies the existence of a new short-range interaction parameter, N_0 , which corresponds to a section of the polymer chain with molecular mass M_0 . Furthermore, the MHS relation is also incompatible with theories

based on the smoothed segment density model. The failure of the latter is due to the fact that (1) the smoothed density model predicts that the number of contacts per segment is proportional to $M^{-1/2}$, while the random-walk treatment predicts that the number of contacts per segment is increasing with M ; and (2) the Flory-Huggins interaction parameter, χ , which describes the thermodynamic behavior of polymer solutions, is assumed to be applicable within a single coil and to be independent of molecular mass.

In view of the foregoing facts, we believe that the present state of theories does not justify attempts to evaluate the interaction parameters from experiments by using either perturbation theories or the smoothed segment density model. It is, therefore, suggested that the three parameters of the MHS relation can be interpreted as follows: K_θ and M_0 are short-range interaction parameters and \underline{a} is a single parameter related to the contact interactions.

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