ring size. It is very small if only small rings (with five to six carbon atoms) are present, but it may become important if the ring formation is a random process. In this case, the average size of the ring (expressed by the number $\bar{k}$ of statistical segments per ring) is given by eq (A.1)

$$\bar{k} = (2^{3/2}/3)N_m{}^{1/2} \qquad \text{(A.1)}$$

where N_m is the number of segments per chain. The intrinsic viscosity, $[\eta]_{0,r}$, of chains with n rings is lower than that of linear molecules, the ratio $g_{0,r}'$ being approximately (at low values of n)

$$[\eta]_{0,r}/[\eta]_{0,1} = g_{0,r}' \simeq 1 - {}^3\!/_2 n(\bar{k}/N_m) \qquad \text{(A.2)}$$

The number of segments N_m is

$$N_m = N/M_0 s$$

where M_0 is the molecular weight of the monomer unit and s stands for the number of monomer units in the segment. Assuming that n is proportional to the molecular weight ($n = \lambda' M$), we obtain from eq (A.2)

$$g_{0,r}' \simeq 1 - {}^3\!/_2 (M_0 s)^{1/2} \lambda' M^{1/2} \qquad \text{(A.3)}$$

On the basis of this equation, the dependence $1/g_{0,r}'$ vs. $M^{1/2}$ has been calculated for S–TCDVB copolymers (with $s = 15$, $M_0 = 104$ and $\lambda' = 4 \times 10^{-6}$) and drawn in Figure 8 (curve 4). Let us compare it with curve 1. In both cases the ratio of the number of tetrafunctional to that of difunctional monomer units in the chain (4 per 10^4) is identical but curve 1 corresponds to a branched structure without intrachain rings, whereas curve 4 corresponds to molecules with rings only. It turns out that the effect of rings (with a random distribution of ring size) on intrinsic viscosity is weaker than that of branched structures but is far from being negligible.

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Intrinsic Viscosity According to Elastic Necklace Model with Hydrodynamic Interaction†

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ABSTRACT: The exact calculation of intrinsic viscosity for the necklace model with up to 300 elastic links and hydrodynamic interaction parameter h^* between 0 and 0.4 shows how slowly with increasing M one reaches the limiting case of impenetrable coil where $[\eta]$ is proportional to $M^{1/2}$. Hence according to the model, a finite $a > 0.5$ can be interpreted as a sign of good solvent only if the measurements are extended over so large a molecular weight range that one is certain that one has already reached the limit of impenetrable coil. The limitation of $h^* = (3/\pi)^{1/2}a_h/b_0$ to values below 0.25 caused most likely by the inadequacy of the linear approximation of Oseen's tensor of hydrodynamic interaction interferes with molecular interpretation of the a_h/b_0 ratio derived from $[\eta]$ as soon as h^* is close to 0.25.

The exact solution[1] of the diagonalization problem of the system of linear partial differential equations describing the density distribution function of the elastic necklace model in linear flow field allows more reliable analysis of the influence of the necklace parameters on the excess stress tensor originating from the presence of the macromolecular coil in a theta solvent. The most investigated component of this tensor is the intrinsic shear stress $[\sigma]_{12} = \lim\,(\sigma - \sigma_s)_{12}/c$ and its gradient coefficient, the intrinsic viscosity $[\eta] = \lim\,(\eta - \eta_s)/c\eta_s = [\sigma]_{12}/\dot{\gamma}\eta_s$. Here c is concentration, $\dot{\gamma}$ is velocity gradient, subscript s relates to solvent, and nonsubscripted quantities relate to solution.

The most important parameters are the number Z of statistically independent ideally elastic links with $Z + 1$ beads, the root mean square link length b_0, and the hydrodynamic radius a_h of bead. The hydrodynamic interaction parameter is $h^* = (3/\pi)^{1/2}a_h/b_0$, the mean-square end-to-end distance $Zb_0{}^2$, and gyration radius $Zb_0{}^2/6$. The former relation is valid from $Z = 1$ on, the latter one from $Z = 2$ on. One can make the number of beads proportional to molecular weight, i.e., $Z + 1 = M/M_0$, where M_0 is the molecular weight of a bead. One will adhere to this choice in that which follows. But one puts often Z proportional to M so that each link corresponds to the same molecular weight M_0. The difference between the two choices does not matter very much at high Z but is very marked at small Z. The model containing one single link has in the former case a molecular weight $2M_0$ but only M_0 in the latter case.

The very modest quantitative information about the amount and effects of coil deformation in flow severely restricts the reliable range of gradient dependence investigation to the limit of zero gradient, $\dot{\gamma} \to 0$. This includes the wide spectrum of dynamic viscosity with the frequency ω ranging from 0 to ∞. On both ends one has a Newtonian range where the viscosity is independent of frequency. In the lower range, $\omega \to 0$, the first Newtonian viscosity $[\eta]_0$ is higher than in the

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† Dedicated to M. L. Huggins on his 80th birthday.

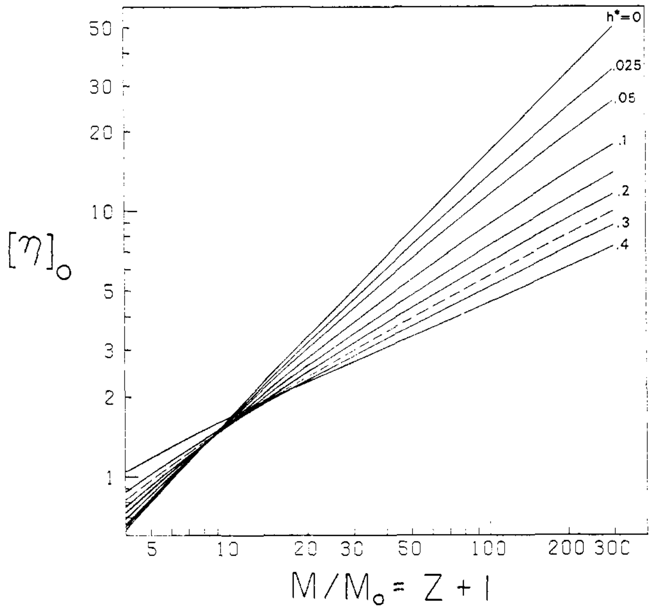

Figure 1. Intrinsic viscosity $[\eta]/B$ as a function of $M/M_0 = Z + 1$ for different h^* from free-draining coil, $h^* = 0$, to complete solvent immobilization at $h^* = 0.25$ (broken line) and beyond that, $h^* = 0.3$ and 0.4. Theta solvent.

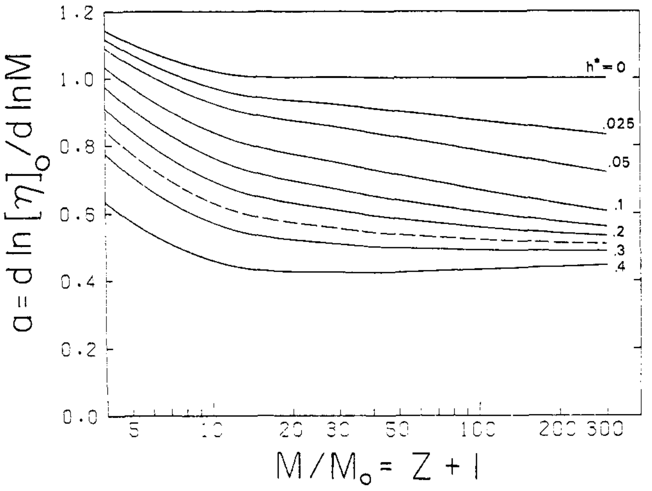

Figure 2. Slopes of a log $[\eta]$ over log M plots as shown in Figure 1.

upper range, $\omega \to \infty$, with the second Newtonian viscosity $[\eta]_\infty$. In the perfectly flexible necklace model without any internal viscosity $[\eta]_\infty = 0$. Any type of rigidity, however, yields a finite $[\eta]_\infty \neq 0$.

The steady state viscosity $[\eta]_0$ at zero gradient and frequency is independent of coil rigidity. This is understandable because in the limit of zero gradient and frequency the infinitely slow shape changes of the coil caused by the flow are completely describable by Brownian motion. The coil has practically the same conformational distribution as in the liquid at rest. Any modification of the model by explicit introduction of internal viscosity does not affect the bead density distribution and its effect on the excess shear stress and hence on intrinsic viscosity.

$$[\eta]_0 = (RT/M\eta_s)\sum_{p=1}^{Z}\tau_p = (\pi N a_h b_0^2/M_0)(Z+1)^{-1}\sum\lambda_p^{-1} = B(Z+1)^{-1}\sum\lambda_p^{-1} \quad (1)$$

$$\tau_p = 1/4\mu D\lambda_p$$

$$\mu = 3/2b_0^2$$

$$D = kT/f = kT/6\pi a_h\eta_s$$

$$B = (\pi N a_h b_0^2/M_0)$$

Hence $[\eta]_p$ depends only on Z and h^* through the eigenvalues λ_p of the tensor **HA**. Here **H** is the tensor of hydrodynamic interaction and **A** that of ideally elastic link forces. For their definition, see ref 1 or the original paper by Zimm.[2] Reference 1 also gives the computer program for calculation of λ_p for any Z and h^*.

In Figure 1 one has plotted $[\eta]/B = (Z+1)^{-1}\,\Sigma\lambda_p^{-1}$ for $h^* = 0$, 0.25, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, and 0.4 versus Z between 3 and 300 corresponding to M/M_0 between 4 and 301. The highest value for Z is the maximum value which with the presently available computers and financial possibilities still permits a reasonable calculation of eigenvalues λ_p.

The calculated intrinsic viscosities are highest for $h^* = 0$ and decrease with increasing h^*, i.e., with decreasing permeability of the coil. The curves can be approximated by the Kuhn–Mark–Houwink equation

$$[\eta] = KM^a = K'(Z+1)^a \quad (2)$$

if one admits slight variation of a with M or Z. Such a variation is to be expected in the range of small Z which represents the transition from the almost free-draining, $a = 1$, to completely impermeable coil, with $a = 0.5$. This range, however, turns out to be much larger than normally expected.[3]

The power a is defined by

$$a = \mathrm{d}\log[\eta]/\mathrm{d}\log M = \mathrm{d}\log[\eta]/d\log(Z+1) \quad (3)$$

The values are plotted in Figure 2 for the same parameters h^* as in Figure 1. The results are as expected. But one is surprised about the slow approach to the limiting value 0.5 which has to be reached for any finite parameter h^* of hydrodynamic interaction in the limit of high Z. The calculated values a are above 0.5 for all h^* equal or below 0.25 and are smaller than 0.5 for higher values of h^*. The separation agrees with the statement that the fully impermeable coil of Zimm corresponds to $h^* = 0.25$. The recalculation of Zimm's integrodifferential equation by Lodge and Wu[4] has indeed shown that at $h^* = 0.25$ the flow immobilization is complete. According to Zimm this corresponds to absolute predominance of hydrodynamic interaction. Hence any h^* values beyond that seem to surpass the validity range of the first term of Oseen's approximation for hydrodynamic interaction which is used in the necklace model. Such a value yields an unrealistic power a below 0.5, i.e., a more than impermeable coil which obviously does not make any sense. The limit $h^* = 0.25$ means a hydrodynamic radius $a_h = 0.256b_0$. Models with smaller a_h/b_0 ratio are permitted but not those with a larger ratio.

Experimentally one mainly deduces a from intrinsic viscosity data of at least two samples with as much different molecular weight as possible

$$\langle a\rangle = \log([\eta]_2/[\eta]_1)/\log(M_2/M_1) \quad (4)$$

By choosing $M_2/M_0 = 301$ and $M_1/M_0 = 4$, 11, 31, 101, one obtains values given in Table I. They show very much the same dependence on Z and h^* as the differential values plotted in Figure 2, i.e., a very slow approach to limiting values corresponding to $Z \to \infty$. The so-calculated power a varies between 0.43 and 1.01 and, as a rule, does not converge rapidly to the limit 0.5. The deviations are quite appreciable up to $Z_1 = 100$. Not even the case $h^* = 0.25$ is a good exception. It does not yet yield $a = 0.5$ even at the highest Z_1. With smaller h^* the average slope is higher and with larger h^* it is smaller than the predicted value for completely impermeable coil in spite of the fact that in all cases the mean-square end-to-end dis-

Table I
The Average Kuhn–Mark–Houwink Coefficients $\langle a \rangle$ as a Function of h^* and Z Range

		h^* =								
Z range	M_1/M_2	0	0.025	0.05	0.1	0.15	0.2	0.25	0.3	0.4
3–300	75.25	1.015	0.924	0.854	0.754	0.685	0.630	0.581	0.536	0.453
10–300	27.36	1.003	0.896	0.816	0.708	0.639	0.587	0.543	0.505	0.434
30–300	9.71	1.000	0.876	0.785	0.673	0.608	0.563	0.526	0.493	0.434
100–300	2.98	1.000	0.852	0.750	0.635	0.579	0.544	0.514	0.488	0.441

tance and gyration radius are strictly proportional to the number of Z links, i.e., to $(M/M_0 - 1)$.

With $h^* < 0.25$ one may explain the deviations as a consequence of the finite flow penetration depth according to Debye–Bueche.[5] As long as it is larger than the coil radius the coil has not yet an impenetrable core which is expected to yield 0.5 for a. From Figure 1 one gets the impression that for $h^* < 0.25$ such a situation prevails up to and even beyond $Z = 300$. Usually a positive difference $a = 0.5$ is considered as a sure indication of a good solvent and coil expansion beyond the unperturbed dimensions. But the wide range of Z over which one finds a relatively constant $a > 0.5$ makes one rather cautious in any such conclusion.

The usual correlation of $a > 0.5$ with the excess coil expansion in a good solvent described by the mean-square gyration radius $R^2 \sim M^{1+\epsilon}$ with $\epsilon = (2a - 1)/3$ certainly cannot be based on the necklace model with hydrodynamic interaction in the whole range of M from oligomers to very high degree of polymerization. Figures 1 and 2 and Table I very convincingly demonstrate that according to the model such a molecular weight dependence of intrinsic viscosity can be caused up to very high Z by a small value $h^* < 0.25$ even in the case that the coil dimensions are exactly those of a random walk coil as assumed in a theta solvent, i.e., $R^2 \sim M$ and $\epsilon = 0$. Hence in a wide range of M any observed a between 0.5 and 1.0 could be the consequence of any one of both effects, excess coil expansion with $\epsilon > 0$ or small hydrodynamic interaction $h^* < 0.25$, or of both acting together. But one cannot exclude in advance any one of them or decide about the ratio of their contribution if one has no other information about the polymer–solvent system and/or the data do not extend over an extremely wide range of M so that one is certain that a has already reached its limiting value.

The smaller than 0.5 values of a for $h^* = 0.3$ and 0.4 are still a little stranger. Since $a = 0.5$ corresponds to a completely impermeable coil with mean-square gyration radius $R^2 \sim M$ one has to do here with a surpassing of the limit. Hence with such a high h^* the model and the eigenvalues seem to be already beyond their useful range. The failure of the model at high h^* seems to be primarily a consequence of the use of Oseen's first-order approximation which does not properly describe the hydrodynamic interaction as soon as the hydrodynamic radius of the bead approaches one-fourth of the link length. Very likely the ratio a_h/b_0 has to be equal to or less than 0.256 in order to keep the error within acceptable limits. One certainly has molecules where a_h is larger than $b_0/4$. They cannot be adequately represented by the necklace model since the $[\eta]$ values for $h > 0.25$, e.g., 0.3 and 0.4, increase too slowly with M. Hence one also cannot expect the experiments to yield a realistic estimate for a_h/b_0 as soon as this ratio derived from geometrical parameters of the linear macromolecule would yield values larger than 0.256.

The situation does not change very drastically if one chooses Z, i.e., the number of links, proportional to molecular weight. For $h^* = 0.25$ the slope turns out to be almost exactly equal to 0.5 in the whole range from $Z = 20$ on. All slopes a start with smaller values and either steadily increase ($h^* > 0.25$) or go first to a maximum and later decrease toward 0.25 ($h^* < 0.25$). Just this maximum and the low initial values of a at the smallest $Z = 3$ seem to be in poor agreement with experimental data on paraffins[6] which show the steepest slope at lowest M.

Conclusions

From this short analysis one can derive some conclusions about the usefulness and limitations of the necklace model for the description of hydrodynamic properties of isolated randomly coiled linear macromolecules in solution and about the molecular interpretation of parameters calculated from intrinsic viscosity. First, the limitation of h^* to values up to 0.25 makes the model inapplicable for the description of hydrodynamic properties as soon as the geometrical dimensions of polymer molecule would yield a ratio a_h/b_0 higher than 0.256. Vice versa in such a case the molecular interpretation of a_h and b_0 becomes unrealistic as soon as h^* approaches the limit 0.25. Second, a value of a between 0.5 and 1.0 can be interpreted as an indication of a good solvent only if Z is so high that one is certain that one has already reached the assymptotic dependence of $[\eta]$ on M. This can be a severe limitation with relatively extended chains having a high M.

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