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Mark−Houwink−Kuhn−Sakurada Exponent at the Θ Condition. Its Invariancy with Respect to the Cross-Sectional Dimensions of Polymer Chains

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ABSTRACT: The question raised by Fujita has been examined, namely why the intrinsic viscosity of many polymers at the Θ condition $[\eta]_0$ is proportional to $M^{1/2}$ over a broad range of molecular weights. An explanation is proposed, based on a combination of the theory of the wormlike cylinder model with reported data on cross-sectional dimensions of 30 polymers with the carbon backbone differing in both the size and type of side groups (vinyl polymers, polyacrylates, polymethacrylates). The behaviors of poly(dimethylsiloxane) and poly(ethylene oxide), which are not in line with this explanation, are briefly discussed.

Introduction

The classical theory of the intrinsic viscosity of random coils at Θ conditions $[\eta]_0$ (cf. ref 1) predicts the quotient $a_0 \equiv \mathrm{d}\ln[\eta]_0/\mathrm{d}\ln M$ to decrease from unity to $^1/_2$ as the chain length increases. The proportionality between $[\eta]_0$ and $M^{1/2}$ (i.e., $a_0 = {}^1/_2$) is obtained as a limiting law for the nondraining regime.

An experimental fact, which is at variance with the above prediction, is that for many polymers in Θ solvents the exponent a_0 is equal or close to $^1/_2$ over a very broad range of molecular weights. This fact can be explained in terms of theories based on the wormlike cylinder or touched-bead models[2,3] if the reduced chain diameter d_r is 0.4. Here d_r is defined as

$$d_r = d/\lambda^{-1} \qquad (1)$$

i.e., the ratio of the effective hydrodynamic chain diameter d and the Kuhn statistical segment length λ^{-1}. However, as pointed out by Fujita,[4,5] it is amazing that “the values of d_r happen to be nearly the same for any combination of polymer and Θ solvent”.

In this appear we seek an answer to this question by combining the results of the above-mentioned theories with approximate values of d_r for 30 polymers usually referred to as flexible.

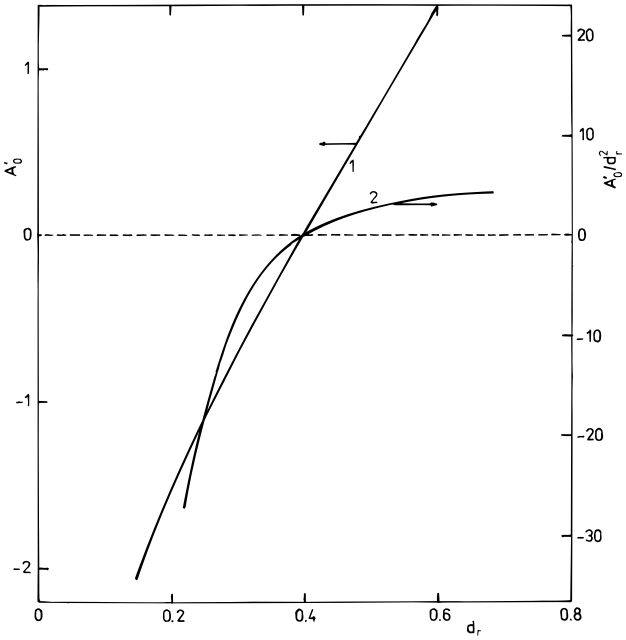

Figure 1. Dependences on the reduced chain diameter d_r of the parameter A'_0 in eq 4 (curve 1) and the ration A'_0/d_r^2 (curve 2).

Discussion

The intrinsic viscosity of the wormlike cylinder at the Θ condition is written

$$[\eta]_0 = [\Phi_{0,\infty}(\langle R^2\rangle_0/M)_\infty^{3/2}M^{1/2}]\Gamma(L_r,d_r) \qquad (2)$$

where $(\langle R^2\rangle_0/M)_\infty$ is the random coil limit of the ratio of the “unperturbed” mean-square end-to-end distance and molecular weight, $\Phi_{0,\infty}$ is the Flory constant in the nondraining regime, the reduced contour length (or the number of Kuhn segments per chain) is

$$L_r = M/(M_L\lambda^{-1}) \qquad (3)$$

and M_L is the shift factor, which is currently set equal to the molecular weight per unit chain contour length. Exact values of the $\Gamma(L_r,d_r)$ function have been tabulated.[2] Several simple approximations to this function have been proposed[6,7] to facilitate the treatment of experimental data. We employ the simplest one[7]

$$\Gamma = 1 + A'_0/L_r^{1/2} \qquad (4)$$

where A'_0 is a function of d_r. Equation 4 agrees well with the exact function for $d_r > 0.1$ down to very low values of L_r. The A'_0 values have been tabulated[7] and are plotted against d_r in Figure 1 (curve 1).

From eqs 1−4 we obtain

$$[\eta]_0 = A'_\eta + K_0M^{1/2} \qquad (5)$$

and

$$a_0 \equiv \mathrm{d}\ln[\eta]_0/\mathrm{d}\ln M = (1/2)(1 + A'_\eta/K_0\, M^{1/2})^{-1} \qquad (6)$$

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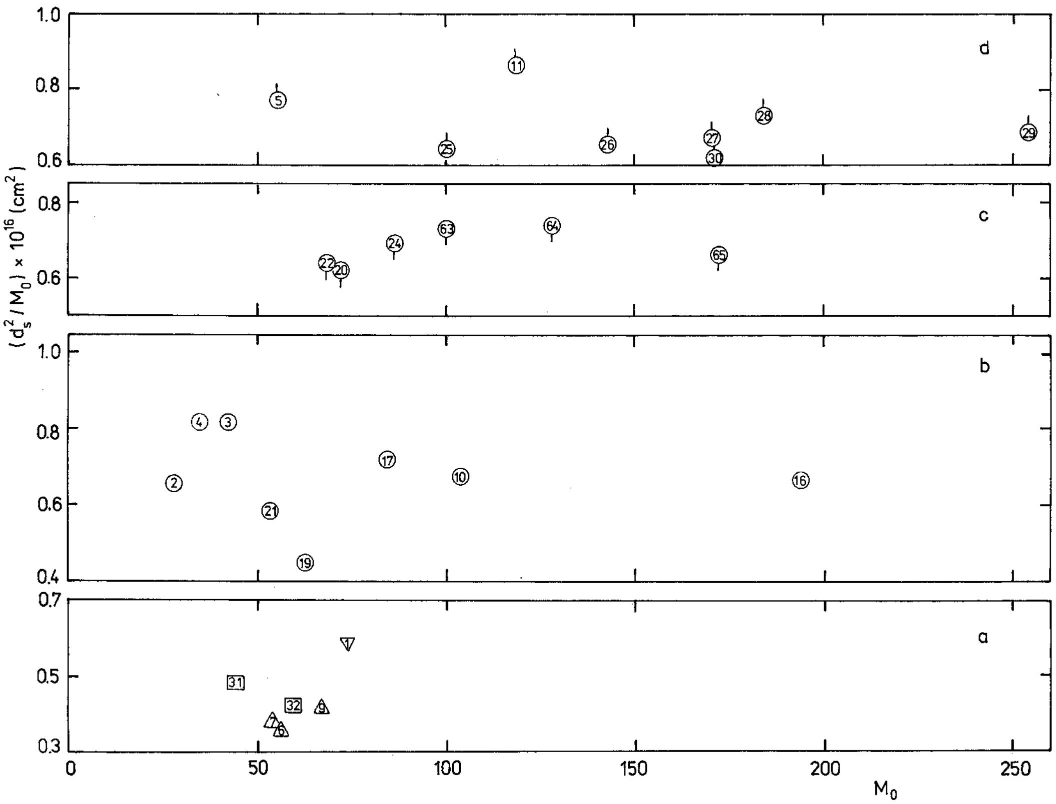

Figure 2. Dependences of the values of d_s^2/M_0 on the molecular weight M_0 of the monomeric unit. Polymers: (a) (□) polyethers, (△) polydienes, (▽) PDMS; (b) (○) vinyl polymers $-CH_2CHX-$; (c) polyacrylics; (d) polymers $-CH_2C(CH_3)R-$. Numbers affixed to data points are those of Tables I and II in ref 8: (1) poly(dimethylsiloxane) (PDMS), (2) polyethylene, (3) polypropylene, (4) hydrogenated polyisoprene, (5) polyisobutylene, (6) *cis,trans*-polybutadiene, (7) *cis*-polybutadiene, (9) *cis*-polyisoprene, (10) polystyrene, (11) poly(α-methylstyrene), (16) poly(*N*-vinylcarbazole), (17) poly(vinyl acetate), (19) poly(vinyl chloride), (20) poly(acrylic acid), (21) poly(acrylonitrile), (22) polyacrylamide, (24) poly(methyl acrylate), (25) poly(methyl methacrylate), (26) poly(butyl methacrylate), (27) poly(hexyl methacrylate), (28) poly(octyl methacrylate), (29) poly(dodecyl methacrylate), (30) poly(2-ethylbutyl methacrylate), (31) poly(ethylene oxide), (32) poly(propylene oxide), (63) poly(ethyl acrylate), (64) poly(butyl acrylate), (65) poly(2-ethylhexyl acrylate).

where

$$K_0 = \Phi_{0,\infty}(\langle R^2\rangle_0/M)_\infty^{3/2} \qquad (7)$$

$$\lambda^{-1} = (\langle R^2\rangle_0/M)_\infty M_L \qquad (8)$$

and

$$A'_\eta = \Phi_{0,\infty}A'_0(\lambda^{-1})^2/M_L \qquad (9)$$

Equations 5 and 6 show that the ratio $[\eta]_0/M^{1/2}$ can be constant and the quotient a_0 equal to $^1/_2$ over the entire range of molecular weights only if the parameter A'_η is equal to zero.

Most of the polymers where the proportionality of $[\eta]_0$ and $M^{1/2}$ exists over a broad span of molecular weights are vinyl polymers and derivatives of poly(acrylic acid) and poly(methacrylic acid) with various side groups. Increasing the size of the substituent increases the cross-sectional chain diameter and, at the same time, the mean molecular weight M_0 per monomeric unit. Assuming that the shift factor M_L for these chains is approximately equal to the molecular weight per unit contour length of the chain in an all-trans conformation at full extension, we can replace M_L by $M_0 l$, where l is the length of the projection of the monomeric unit on the contour. For chains with a C−C backbone, the length l is constant.

It is useful to substitute for λ^{-1} in eq 8 from eq 1 and to rearrange the result into the form

$$\xi \equiv (A'_\eta/\Phi_{0,\infty}l) = (A'_0/d_r^2)(d^2/M_0) \qquad (10)$$

showing that the A'_η parameter and the quotient a_0 depend on the values of (A'_0/d_r^2) and (d^2/M_0).

The former factor is evaluated from theory.[3,7] As shown in Figure 1 (curve 2), its values are negative for $d_r < 0.4$ and very rapidly increase to zero as d_r approaches 0.4. For $d_r > 0.4$ they are positive but, which is particularly remarkable, their further increase with d_r is very slow.

The factor d^2/M_0 is estimated from the values of λ^{-1} and d_s (for polymer solids) tabulated by Aharoni.[8] We are aware that the d_s values for polymers in the solid state need not be those for dissolved chains. However, we believe that by employing Aharoni's data, we gain an insight into the dependence of d on the size of the substituent.

In Figure 2 the values of d_s^2/M_0 are plotted against M_0 for several polymers: polydienes (panel a), vinyl polymers (b), derivatives of poly(acrylic acid) (c), and polymers of type $-CH_2C(CH_3)R-$, where R = CH_3, phenyl, and $COOC_nH_{2n+1}$(d). Numbers affixed to data points are those in Tables I and II of ref 8. It is seen that the values for group (a) are between 0.3 and 0.6 whereas those for the other groups are higher, between 0.6 and 0.8. However, no dependence on M_0 is visible in either group.

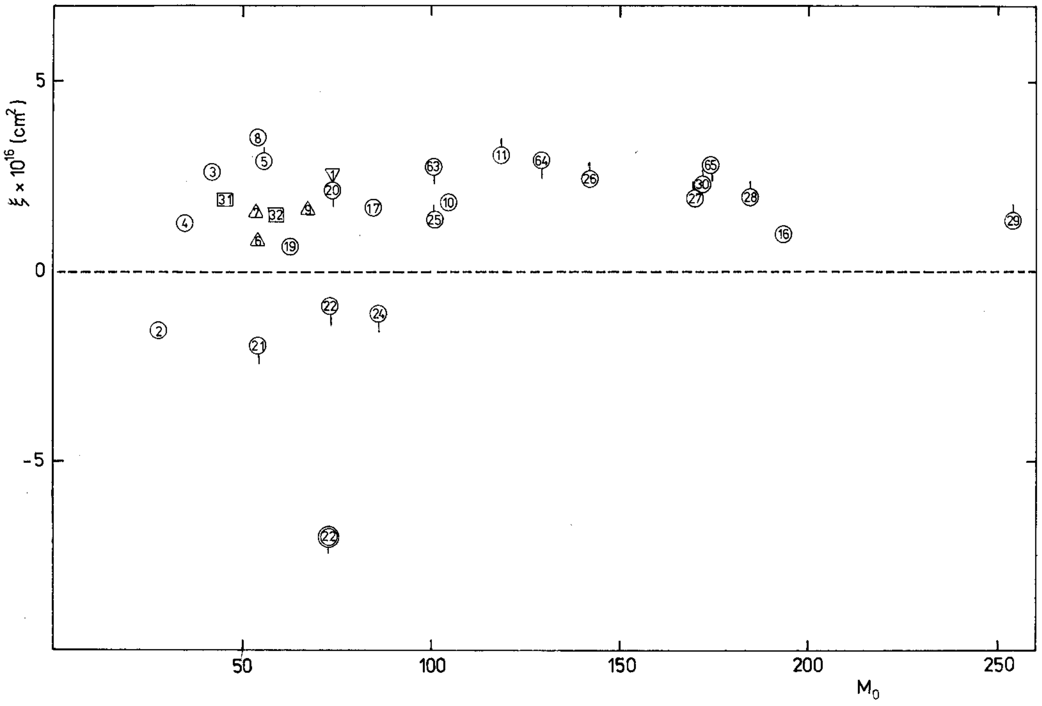

Figure 3. Plot of the parameter ξ as a function of the molecular weight M_0 of the monomeric unit. Data notation is the same as in Figure 2.

Figure 3 shows that the ξ parameter for 26 polymers is positive and, which is relevant for the present discussion, does not display any distinct dependence on M_0, i.e., on the size of the substituent. This invariance is remarkable in particular with polymethacrylates where M_0 varies between 100 and 254 (methyl and dodecyl esters, code numbers 25 and 29) and with vinyl polymers where $35 \leq M_0 \leq 193$ (hydrogenated polyisoprene and poly(N-vinylcarbazole), code numbers 4 and 16).

The invariance of ξ can account for the fact that, in spite of large differences in structure, the molecular weight dependences of $[\eta]_0$ for these polymers are very similar. However, since the ξ and A'_η values differ more or less from zero, the quotient a_0 cannot be constant and equal to $^1/_2$ over the entire span of molecular weights. Positive or negative deviations from $a_0 = {}^1/_2$ can be expected at low molecular weights.

It follows from eq 6 that for $\xi > 0$ the logarithmic plot of $[\eta]_0$ vs M should be slightly convex with respect to the axis of the abscissa at low molecular weights and approach the asymptotic shape with slope $^1/_2$ at high ones. The region where the asymptotic behavior is attained depends on the values of A'_η and K_0 and, therefore, on the structure of the polymer. The shape of plots of log $[\eta]$ vs log M predicted for chains with positive ξ has indeed been observed with polystyrene,[9] polyisobutylene,[10] poly(methyl methacrylate),[11] and poly(vinyl acetate)[12] (code numbers 10, 5, 25, and 17). We content ourselves with this qualitative conclusion and do not pursue the discussion in quantitative terms because, as has been shown recently,[9–11,13] other factors not accounted for in the theory of the wormlike cylinder (e.g., loose helical conformations) may take the hydrodynamic behavior more involved at low molecular weights.

Let us now consider the few polymers with $\xi < 0$. The logarithmic plots of $[\eta]_0$ vs M should be concave with respect to the M axis at low M. This has indeed been established with polyethylene.[14,15] A very strong curvature would be expected with polyacrylamide (code number 22 with double ring in Figure 3) if the value of $\xi = -7 \times 10^{-16}$ cm^2 were correct. However, the λ^{-1} value quoted in ref 8 ($\lambda^{-1} = 24 \times 10^{-8}$ cm) has been estimated from good-solvent data. A more recent value, $\lambda^{-1} = 18 \times 10^{-8}$ cm, obtained in a mixed Θ solvent[16] is lower by 25%. With this value the data points for this polymer in Figures 2 and 3 are shifted to $d_r = 0.37$ and $\xi = -1 \times 10^{-16}$ cm^2, respectively. From the latter value and $K_0 = 0.13$ cm^3/g (cf. ref 16), we obtain $A'_\eta = -0.7 \times 10^{-16}$ cm^2. In Figure 4 the experimental data for polyacrylamide are compared with the curve calculated using eq 5 and the above parameter values. The dashed straight line is an extension to low molecular weights of the dependence for $M > 10^5$ where $a_0 \simeq 0.5$. The difference between the calculated and experimental values is within the limits of experimental accuracy.

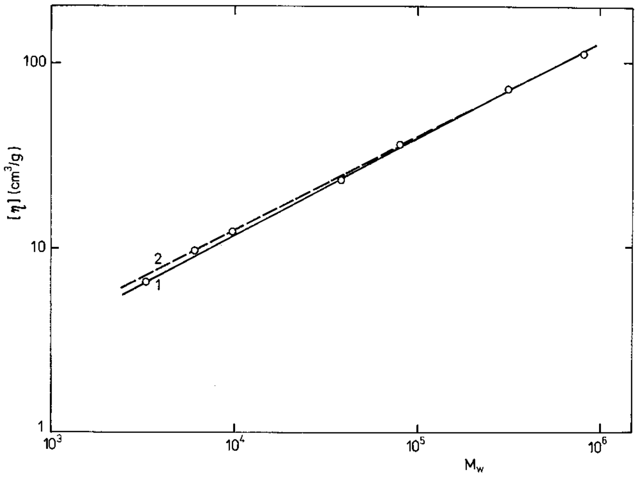

Figure 4. Logarithmic plot of $[\eta]_0$ vs M_w for polyacrylamide in Θ solvent (water–methanol, 3:2 parts of volume) at 20 °C. Data from ref 16. Curves: (1) calculated using eq 5 and $A'_0 = -0.71$, $K_0 = 0.127$ cm^3/g; (2) asymptotic dependence with slope $a_0 = {}^1/_2$.

No data at low molecular weights in Θ solvents are available for the other two polymers with $\xi < 0$ [poly(acrylonitrile) and poly(methyl acrylate), code numbers 21 and 24]. By analogy with polyacrylamide, we may expect that nonlinearity of the logarithmic plot of $[\eta]_0$ vs M at low molecular weights will not be strong.

Poly(dimethylsiloxane) and poly(ethylene oxide) (code numbers 1 and 31) do not belong to the same category of polymers as those discussed above. Nevertheless, their behavior is worth a brief comment. Positive values of ξ for both of them would imply similarity of the plots of $[\eta]_0$ vs M to those for polystyrene. However, the opposite behavior has been established with the former. The d_r values[17] are considerably lower than 0.4, and the chain diameter d is remarkably smaller as compared to that for other polymers. This finding has been confirmed by Yamada et al.[13] from an analysis of transport data on the basis of the helical wormlike model.

With poly(ethylene oxide) the shape of the plots of $[\eta]_0$ vs M at low molecular weights depends on the solvent.[18,19] While the plots for aqueous salt solutions at the Θ condition correspond to $\xi > 0$ and $d_r > 0.4$ (in agreement with expectation), those in organic Θ solvents correspond to $\xi > 0$ and $d_r > 0.4$. The reason for this difference is not yet clear.

Conclusions

It has been shown that, with most vinyl type polymers, polyacrylates and polymethacrylates, the reduced cross-sectional diameter of the chain d_r varies with the size of the side groups in the range ($0.35 \lesssim d_r \lesssim 0.8$), where a variation in d_r has little effect on the intrinsic viscosity at Θ conditions $[\eta]_0$. This finding may explain the experimental fact that, with most polymers of these groups, the intrinsic viscosity $[\eta]_0$ is proportional to $M^{1/2}$ over a very broad range of molecular weights, irrespective of the size and type of the side group. More significant effects of the diameter on $[\eta]_0$ and the quotient a_0 can be expected if $d_r < 0.4$, i.e., with thin and/or very stiff chains.

References and Notes

(1) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
(2) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.
(3) Yoshizaki, T.; Nitta, I.; Yamakawa, H. *Macromolecules* **1988**, *21*, 165.
(4) Fujita, H. *Macromolecules* **1988**, *21*, 179.
(5) Fujita, H. *Polymer Solutions*; Elsevier: Amsterdam, 1990.
(6) Bohdanecký, M. *Macromolecuels* **1983**, *16*, 1483.
(7) Bohdanecký, M.; Netopilík, M. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 383.
(8) Aharoni, S. M. *Macromolecules* **1986**, *19*, 426.
(9) Einaga, Y.; Koyama, H.; Konishi, T.; Yamakawa, H. *Macromolecules* **1989**, *22*, 3419.
(10) Abe, F.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1991**, *24*, 1608.
(11) Fujii, Y.; Tamai, Y.; Konishi, K. J.; Yamakawa, H. *Macromolecules* **1991**, *24*, 1608.
(12) Ueda, M.; Kajitani, K. J. *Makromol. Chem.* **1967**, *108*, 138.
(13) Yamada, T.; Koyama, H.; Yoshizaki, T.; Einaga, Y.; Yamakawa, H. *Macromolecules* **1993**, *26*, 2566.
(14) Chiang, R. *J. Phys. Chem.* **1965**, *69*, 1645.
(15) Chiang, R.; Zakin, J. L.; Mayhan, K. G. *J. Appl. Polym. Sci.* **1983**, *184*, 2061.
(16) Bohdanecký, M.; Petrus, V.; Sedláček, B. *Makromol. Chem.* **1983**, *184*, 2061.
(17) Bohdanecký, M.; Petrus, V.; Horská, J.; Edwards, C. J. C.; Stepto, R. F. T. *Makromol. Chem.* **1988**, *189*, 1865.
(18) Beech, D. R.; Booth, C. *J. Polym. Sci., Part A-2* **1969**, *7*, 575.
(19) Bohdanecký, M.; Kovář, J.; Fortelný, I. *Polymer* **1979**, *20*, 813.

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