Partial draining of low-molecular weight polymers with flexible chains

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(Received 22 January 1979)

The results of the theory of intrinsic viscosity based on the model of a worm-like chain have been used in analyses of the $[\eta]$–M correlation under theta conditions, and of the Stockmayer–Fixman plot for polymers with flexible chains at molecular weights $M < 10^5$. Their viscosity behaviour appears to be influenced by the chain thickness d. An analysis of the available data allowed us to obtain reasonable d values for several polymers: polyethylene; poly(ethylene oxide); polystyrene; poly(methyl methacrylate), and poly(vinyl acetate). The effect of solvent on d was ascertained. The analysis shows that the reliability of the results obtained by the Stockmayer–Fixman method is the higher, the larger the proportion of data used which reside in the region $M > 10^5$.

INTRODUCTION

Correlation of intrinsic viscosity and molecular weight treated on the basis of the Stockmayer–Fixman plot, $[\eta]/M^{1/2}$ vs.. $M^{1/2}$, has some special features in the case of polymers with flexible chains in the range of low molecular weights (of the order 10^4 and less)[1–4], thus: (a) under theta conditions, the $[\eta]_\theta/M^{1/2}$ values are rarely constant for very low molecular weights; compared with the limiting value

$$\lim_{M\to\infty} [\eta]/M^{1/2} = K_0$$

they are either lower (polyethylene[5,6], poly(ethylene oxide)[7]) or higher (polystyrene[8,9]); (b) at low M, the $[\eta]/M^{1/2}$ vs. $M^{1/2}$ dependences of good solvents are curved either downwards (polyethylene[5,6], polyethylene oxide[7,10–12]) or upwards (e.g., poly(methyl methacrylate), *cf.* data in reference[13]); (c) the region in which such deviations occur depends on both the polymer and the solvent.

According to a qualitative interpretation[1–4,14], these special properties are connected with the following factors: (1) the ratio of the mean square chain end-to-end distance to the molecular weight in the state unperturbed by excluded volume is lower at low molecular weights than its limiting value

$$\lim_{M\to\infty} (\bar{R}_0^2/M) \equiv (\bar{R}_0^2/M)_\infty \;;$$

(2) partial draining of the macromolecular coil is operative; (3) the contribution of the individual chain hydrodynamic subunits to the intrinsic viscosity, which follows from their incompressibility and inability to rotate under the conditions of laminar flow, is not negligible[4,14]; (4) Specific interaction of solvent molecules with chain segments, and especially with endgroups of the polymer chain, occurs in this case[1,2,4].

According to the theories which describe a macromolecule as an assembly of point frictional centres[15,16] and with respect to phenomena (1) and (2) above, $[\eta]_\theta/M^{1/2}$ in the low-molecular weight range must always be lower than K_0. To explain the case $[\eta]_\theta/M^{1/2} > K_0$, an assumption which is not completely consistent with these theories has to be used (3). Recently, a theory has been put forward which contemplates a finite chain thickness in the hydrodynamic description[17]. According to this theory, both cases, namely, $[\eta]_\theta/M^{1/2} \gtrless K_0$, may occur, depending on the relative chain thickness.

In this paper we examine the application of this theory to quantitative interpretation of (a), (b) and (c).

THEORY

In the theory of Yamakawa and Fujii[17], the macromolecule is represented by a flexible cylinder having diameter d and contour length L. Its flexibility is characterized by the length of a statistical segment, l, and the statistics of the wormlike chain. It follows from the theory of such a model that[16]

$$l/M_L = \lim_{M\to\infty} (\bar{R}_0^2/M) \equiv (\bar{R}_0^2/M)_\infty \tag{1}$$

The relationship between the contour length and molecular weight M (or the number of bonds in the chain, n) is expressed through[17,18]

$$M = M_L L \tag{2}$$

$$n = fL/l \tag{3}$$

where M_L and f are 'shift factors'. M_L is defined as the molecular weight per unit of contour length. For the intrinsic viscosity under theta conditions, the theory gives

$$[\eta]_\theta = \Phi_0(Ll)^{3/2}/M \tag{4}$$

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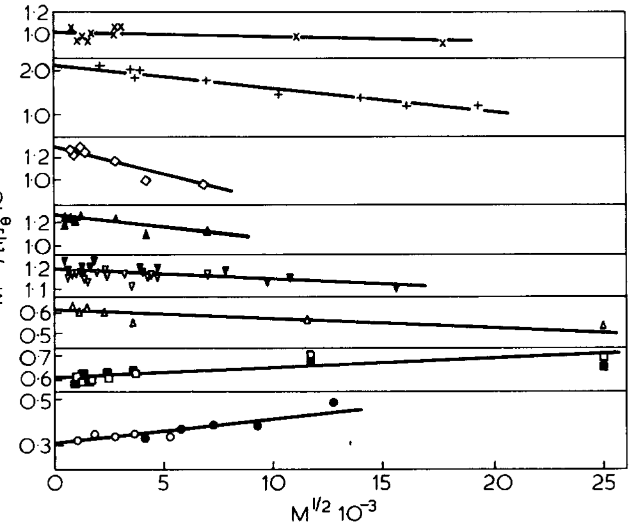

Figure 1 Treatment of viscosity data using equation (10). Literature data: polyethylene diphenyl ether[5,6] ○, ●; poly(ethylene oxide) – diethyleneglycol diethyl ether[7] □; poly(ethylene oxide) – methyl isobutyl ketone[7] ■; poly(ethylene oxide) – 0.45-M aqueous potassium sulphate[7] △; polystyrene-cyclohexane[8,9] ▽, ▼; polystyrene-decalin[9] ▲; polystyrene-dioctyl phthalate[9] ◇, poly(methyl methacrylate)[13] +; poly(vinyl acetate) – methanol[22] x

in which Φ_0 is a function of the reduced length L_r, where $L_r = L/l$, and of the reduced thickness d_r, where $d_r = d/l$. For $L_r \geqslant 20$, Φ_0 may be approximated by[19]

$$\Phi_0 = \Phi_\infty(1 - A_0 L_r^{-1/2}) \tag{5}$$

If $10^{-3} \leqslant d_r \leqslant 1$, 2.87×10^{21}, may be substituted for Φ_∞ (i.e. $\lim \Phi_0$ for $L_r \to \infty$).

The parameter A_0 is connected with the chain length. The theoretical function of Yamakawa and Fujii[17] may be approximated by the simple expression[19]

$$A_0 = -1.23 - 1.97 \ln d_r$$

which is contrary to a theory suggested by Hearst which gives

$$A_0 = -1.28 - 0.891 \ln d_r \tag{6b}$$

The difference between the two functions is considerable[19] especially at $d_r < 1$. By combining equations (1), (2), (4), (5) and $L_r = L/l$, we obtain[19]

$$M/[\eta]_\theta = A_\eta + B_\eta M^{1/2} \tag{7}$$

in which

$$1/B_\eta \equiv K_0 = \Phi_\infty(\bar{R}_0^2/M)_\infty^{3/2} \tag{8}$$

and

$$A_\eta = B_\eta (M_L l)^{1/2} A_0 \tag{9}$$

Equation (7) is the basis of the so-called Hearst plot $M/[\eta]_\theta$ vs $M^{1/2}$, the slope (B_η) and the intercept (A_η) of which can be used to determine the characteristics of chain flexibility $(\bar{R}_0^2/M)_\infty$ and of hydrodynamic interaction, respectively. Experimental data, especially at a low A_η, are more advantageously treated by using the plot $M^{1/2}/[\eta]_\theta$ vs. $M^{-1/2}$, based on a transformation[20,21] of equation (7)

$$M^{1/2}/[\eta]_\theta = B_\eta + A_\eta/M^{1/2} \tag{10}$$

where B_η is the intercept and A_η is the slope.

Figure 1 shows the $M^{1/2}/[\eta]_\theta$ vs. $M^{1/2}$ dependences for polyethylene (PE), poly(ethylene oxide) (PEO), polystyrene (PS), poly(vinyl acetate) (PVAc), and poly(methyl methacrylate) (PMM). The data for the first four polymers were taken directly from original papers[5–9,22]. For PMM, only data for 'good' solvents (benzene, toluene) are available in the range $M < 4 \times 10^4$ [13,23]. In the Stockmayer–Fixman plot (*Figure 2*) they exhibit a very pronounced minimum at $M^{1/2} = 120$–150. We believe that such behaviour may arise from the superposition of two counteracting effects, namely, the excluded volume (which increases with increasing molecular weight) and the effect of partial draining (which decreases with increasing molecular weight). For $\alpha_\eta^3 \leqslant 1.6$, the former effect may approximately be described by the equation[16]

$$[\eta]/[\eta]_\theta = \alpha_\eta^3 = 1 + C_1 z \tag{11}$$

where the parameter of the excluded volume, z, is proportional to $M^{1/2}$ (for the sake of simplicity, $PM^{1/2}$ is used from here onwards instead of $C_1 z$).

Equations (7), (11) yield

$$[\eta]/M^{1/2} = \frac{(1/B_\eta)(1 + PM^{1/2})}{1 + A_\eta/(B_\eta M^{1/2})} \tag{12}$$

The two effects may be separated approximately as follows: Let us construct the plot $[\eta]/M^{1/2}$ vs. $M^{1/2}$ (*Figure 2*) and draw a straight line through the experimental points beyond the minimum, i.e. for $M^{1/2} > 250$, so that the line is directed to the intercept $K_0 = 5 \times 10^{-4}$ (reference 24). From this straight line, $[\eta]/M^{1/2}$ values which would be observed for the polymer in the absence of weaker hydrodynamic interaction are obtained for $M^{1/2} < 250$. These values are then used in the calculation of the expansion factors $\alpha_\eta^3 = [\eta]/K_0 M^{1/2}$. Using the derived α_η^3, approximate values for the intrinsic viscosity under theta conditions, $[\eta]'_\theta = [\eta]/\alpha_\eta^3$, can be determined from the experimental

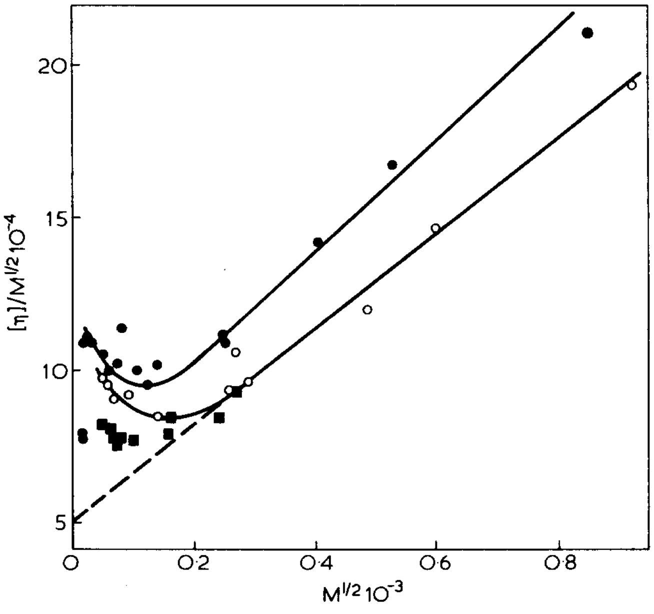

Figure 2 The Stockmayer–Fixman dependence for poly(methyl methacrylate). Benzene: ○ M_w data[13], ● M_n data[13]. Toluene: ■ M_n data[23]

Table 1 Chain thicknesses determined using equation (6a)

Polymer	Solvent	$(1/B_\eta) \times 10^4$	$A_\eta \times 10^4$	d_r	d,Å	Experimental data from references
PE	diphenyl ester	30.3	0.4	0.21	2.4	5.6
PED	MIBK[a], DEGDE[b]	16.4	0.5	0.34	2.7	7
	0.45-M K_2SO_4	16.4	−0.4	1.31	10	7
PS	cyclohexane	8.2	−0.4	0.57	10	8.9
	decalin	7.9	−1.9	0.71	12	9
	dioctyl phthalate	7.6	−4.7	0.94	16	9
PMM	cf. text	5.0	−4.7	0.93	11	13
PVAc	methanol	10	0	0.53	8.7	22

[a] Methyl isobutyl ketone, [b] diethyleneglycol diethyl ether

$[\eta]$ values. These intrinsic viscosity values are then treated according to equation (10).

With PMM, only $[\eta]$ vs. M_w data were used in the analysis, because they are less sensitive to the residual polydispersity of the fractions than is $[\eta]$ vs. M_n relation. The trends of the $[\eta]/M^{1/2}$ vs. $M_n^{1/2}$ plots are quite identical, however (see *Figure 2*). A minimum is also observed in the data on toluene solutions[23]. A dependence similar to that shown by PMM is also observed with the Stockmayer–Fixman plots for polyisobutylene in diisobutylene, constructed according to reference 25, but the minimum is situated at $M^{1/2} \simeq 50$. The procedure for the separation of the excluded volume effect and the hydrodynamic interaction just described is not accurate here, because the non-linearity of the α_η^3 vs. $M^{1/2}$ function has to be neglected, and possible dependence of the coefficient C_1 in equation (11) on the chain length is therefore not taken into account. This approximation does not affect the qualitative value of the conclusions.

The $M^{1/2}/[\eta]_\theta$ vs. $M^{-1/2}$ dependences in *Figure 1* have (with the exception of PVAc) non-zero slopes A_η. The A_η values (*Table 1*), though low, cannot be neglected by comparison with the $B_\eta M^{1/2}$ term in equation (7) at low molecular weights. It follows from equation (6a) that A_0 is positive if $d_r < 0.537$. This means that a positive value from the experimentally available constant A_η (here found for PE, PEO in organic solvents) corresponds to a relative thickness smaller than 0.537, while a negative value (observed for PEO in an aqueous potassium sulphate solution, for PS and PMM) corresponds to a larger thickness. In general features, such order fits in with an elementary idea about the probable chain thickness. The attainment of quantitative data is impeded by the fact that the theories quoted above give rather different $A_0(d_r)$ functions. It seems reasonable, therefore, to attempt the calculation using both methods, and to compare the results obtained.

To calculate the relative thickness using equation (6) and (9), one must know the shift factor M_L (or f). According to Maeda *et al.*[26], for polyethylene and polyethylene oxide a satisfactory M_L can be obtained by regarding the length of the fully extended chain in the trans-conformation as equal to the contour length L. Such a procedure has also been employed for other polymers[27]. We have employed M_L values from these papers[26,27]. The shift factors for PEO and PVAc were calculated employing a similar procedure. In the calculation for PEO, 110° was assumed for both types of valency angle[24], and b = 1.46 Å, i.e. the weighted average bond length of b_{C-C} and b_{C-O}, was taken as the bond length.

The d values (*Table 1*), calculated using equation (6a), are surprisingly close to the dimensions estimated from the van der Waals radii of the individual groups or atoms, and therefore seem reasonable. Calculation using equation (6b) gives unrealistically low values for d (e.g., 0.4 Å for PE). The d values depend on solvent; the differences in A_η for PS in three solvents (and similarly for PEO) are so pronounced that they cannot be neglected.

If data for PEO in benzene compiled from four papers[7,10–12] are treated by the Stockmayer–Fixman plot, one can see that, at $M < 2.5 \times 10^3$, the $[\eta]/M^{1/2}$ values are lower than

$$\lim_{M\to\infty} ([\eta]_\theta/M^{1/2}) \equiv K_0 \text{ (\textit{Figure 3})}.$$

The figure shows schematically the $[\eta]_\theta/M^{1/2}$ vs. $M^{1/2}$ dependence calculated from equation (10) and the relevant parameters are given in *Table 1*. The low $[\eta]/M^{1/2}$ values are obviously connected with the fact that in this range $[\eta]_\theta/M^{1/2} < K_0$. The same behaviour can be observed with PEO in other solvents[10,11] and with polyethylene (data from references 5 and 6), though the amount of experimental data is smaller. In some solvents, however, oligomeric PEO samples exhibit an 'upturn', which, according to Bianchi and Peterlin[4] and others[2,3], is related to interaction between the endgroups of the polymer chain and solvent.

When interpreting *Figure 3*, one should not disregard the possibility that the coefficient C_1 in equation (11) need not be constant when only very low numbers of bonds are present in the main chain. According to the Kurata–Yamakawa theory[28], based on the bead necklace model with a Gaussian chain end distribution, the coefficient C_1 for partly draining molecules is lower than that of nondraining ones. Although for the worm-like chain the theory of hydrodynamic pro-

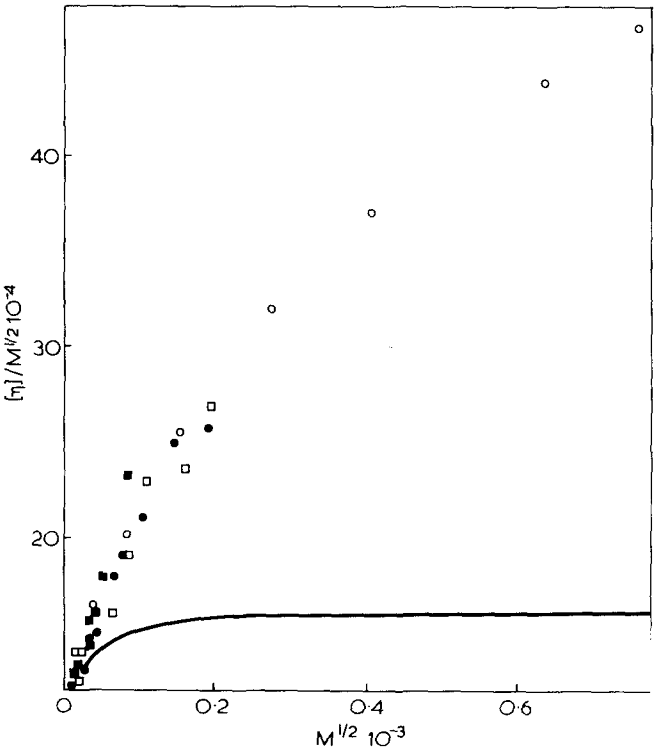

Figure 3 The Stockmayer–Fixman plot for poly(ethylene oxide) in benzene. ○,□,●,■ experimental data from refs[7,10,11,12]. Curve calculated from equation (10) with parameters in *Table 1* for methyl isobutyl ketone (theta solvent)

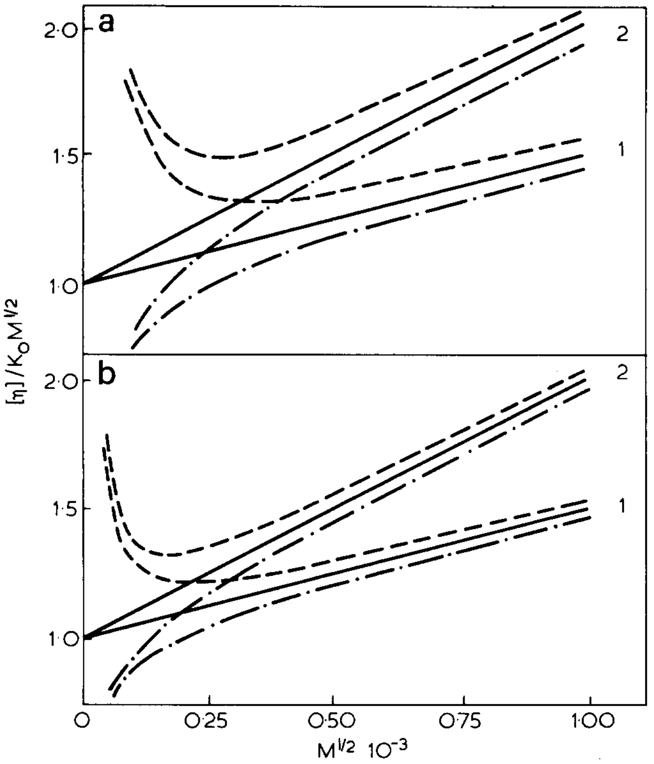

Figure 4 The dependence $[\eta]/K_0M^{1/2}$ vs. $M^{1/2}$ calculated using equation (12). (a) $|A_\eta/B_\eta| = 40$, (b) $|A_\eta/B_\eta| = 40$. Straight lines 1, 2 $A_\eta/B_\eta = 0$, $P \times 10^3 = 0.5$ and 1.0, respectively. Dot-and-dash curves $A_\eta/B_\eta > 0$, dashed curves $A_\eta/B_\eta < 0$

perties of molecules with significant excluded volume has not been formulated in a fashion suitable for this discussion[29], in the relation for the expansion coefficient of the mean square chain end-to-end distance,

$$\alpha_R^2 = 1 + K(L_r)z + \ldots \qquad (13)$$

the coefficient $K(L_r)$ decreases with decreasing reduced contour length according to theory[30]. With respect to these predictions, the coefficient C_1 for the wormlike model may also be lower at low M.

Limitations in the application of the Stockmayer–Fixman method to polymers with flexible chains.

The reliability of the Stockmayer–Fixman method for the determination of unperturbed dimensions (and of similar methods) has been the object of many discussions[1, 31, 32], especially for polymers with stiff chains. Using the results of the preceding discussion, we shall now attempt to define the conditions (mainly with regard to the molecular weight range) under which this method may give satisfactory results for polymers with flexible chains (polyolefins, polyethers, polyesters, polyamides etc.).

The Stockmayer–Fixman method is based on the elimintion of the excluded volume effect by extrapolating $[\eta]/M^{1/2}$ values to $M^{1/2} = 0$. According to the excluded volume theory[30], $K(L_r)$ in equation (13) assumes a non-zero value at $L_r = 1$ and the limiting value $K(\infty) = 134/105$ at $L_r \geqslant 100$. The course of the function $C_1(L_r)$ or $C_1(L_r, d_r)$ in equation (11) is not known, but it may be expected to resemble that of $K(L_r)$. This is probably a less important source of error in the extrapolation method than the effect of partial draining expressed through the parameter A_η. As follows from equation (14),

$$[\eta]_\theta/M^{1/2} = \frac{(1/B_\eta)}{1 + A_\eta/(B_\eta M^{1/2})} \qquad (14)$$

which is obtained from equation (7), this effect, which is expressed through the denominator in the expression is the more important the lower the molecular weight. This indicates that data from the latter range should not be employed in the extrapolation. The upper limit of this range (i.e. the lower boundary of the inverval where $A_\eta/B_\eta M^{1/2} \ll 1$) cannot in general be determined, because A_η depends on the relative thickness d_r.

In the case of polymers with a low d_r (such as polyethylene, poly(ethylene oxide)), $[\eta]_\theta/M^{1/2}$ values converge with increasing molecular weight to the upper limit K_0. Thus, the effect of partial draining operates in the same sense as the excluded volume effect. With these compounds, extrapolation should not be carried out using data for samples in which the number of bonds in the chain $n < 10^3$, because they will not lie in the asymptotic region where $A_\eta/B_\eta M^{1/2}$ can be neglected by comparison with unity and also where the coefficient C_1 is close to its limiting value.

For many polymers in this group (e.g., polyesters, polyamides, polyethers), samples with a sufficiently high number of bonds in the main chain are often difficult to obtain. The risk of inaccurate deductions is then rather considerable and it is the higher the smaller the amount of data above the indicated limit. This may be illustrated by using a model calculation (*Figure 4*). It shows how the Stockmayer–Fixman dependences calculated for $A_\eta/B_\eta = 20$ and 40 relate to those for $A_\eta/B_\eta = 0$. Linear extrapolation from the interval $2 \leqslant M \times 10^{-4} \leqslant 10$ gives a result lower than the correct one by as much as 20%. Extrapolation from the interval $1 \leqslant M \times 10^{-4} \leqslant 4$ would give a still poorer result.

For vinyl polymers with higher d_r, the effects of excluded volume and partial draining are in opposition. If the latter effect is particularly strong, a minimum appears in the Stockmayer–Fixman plot. Its approximate value can be determined from equation (15) derived from equation (12) by assuming that C_1 = constant

$$M_m^{1/2} = -(A_\eta/B_\eta)\ \{1 \pm [1 - (B_\eta/A_\eta P)]^{1/2}\} \qquad (15)$$

If $P > 0$, the minimum may occur only at $A_\eta < 0$. With increasing P (i.e. with increasing 'solvent power') M_m decreases (*Figure 5*). The dependences in *Figure 5* have been calculated assuming that C_1 is constant and that equation (11) is a sufficient approximation for $\alpha_\eta^3 < 3$ to allow us to use it to describe the excluded volume effect. In spite of this, however, it seems desirable to take into account the non-linear form of the α_η^3 vs. z dependence.

Figure 4, in which one can see the $[\eta]/K_0M^{1/2}$ vs. $M^{1/2}$ dependences, calculated for $P \times 10^3 = 0.5$, 1 and for $A_\eta/B_\eta = 0$, –20 and –40, shows how the non-zero value of A_η/B_η affects the Stockmayer–Fixman dependence and extrapolation. Extrapolation from the $M^{1/2} > M_m^{1/2}$ range can be performed linearly, but the intercept on the y-axis (K_0') at $A_\eta/B_\eta = -20$ and –40 is higher by 10% and 20%, respectively, than the correct value. The error is the smaller, the wider range beyond M_m covered by the data. On the contrary, if the molecular weight range is narrow (e.g. $2 \leqslant M \times 10^{-4} \leqslant 16$), the minimum may not be distinct and linear extrapolation of $[\eta]/M^{1/2}$ vs. $M^{1/2}$ can give a result higher by as much as 50%.

Hence, one may conclude that with the polymers discussed in this work or with similar ones, the Stockmayer–Fixman method may provide unreliable K_0 values if the

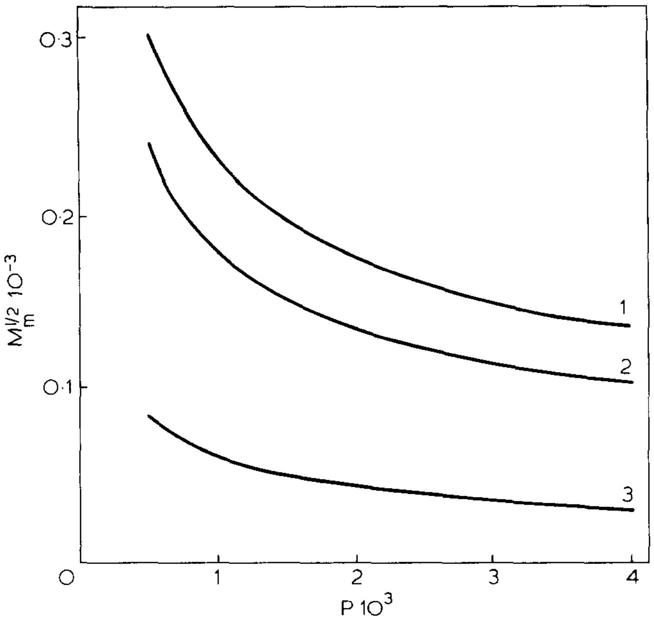

Figure 5 Effect of the polymer–solvent interaction on the position of the minimum in the dependence $[\eta]/M^{1/2}$ vs. $M^{1/2}$ at $A_\eta/B_\eta < 0$. M_m, molecular weight at the minimum; P, interaction characteristic. Curves 1, 2, 3 for $A_\eta/B_\eta = -36; -24; -3.33$, respectively

molecular weights are lower than 10^5. With comparatively thin chains there is a danger that the K_0 value determined by such a procedure would be smaller than the real one, while with polymers with thick chains the reverse would be the case.

Another factor which may affect the Stockmayer–Fixman dependence is the influence of the solvent on the parameter A_η, i.e. on *d*. One may deduce from *Table 1* and *Figure 1* that, e.g. for polystyrene, this influence is considerable. If A_η for PS in dioctyl phthalate were taken as a universal characteristic of the polystyrene chain, the minimum should lie at $M_m^{1/2} \times 10^{-3} = 0.2$–$0.3$. In actual fact, however, PS in benzene, toluene or methyl ethyl ketone up to $M^{1/2} = 0.05$–0.1, exhibits monotonic dependences all correspondingly to an intercept identical with the value observed in θ-solvents. It seems that in these solvents the parameter A_η for polystyrene is close to zero.

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