On the evaluation of unperturbed dimensions from intrinsic viscosity data of binary and ternary polymer solutions*

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Several investigations show that the unperturbed dimensions of a given polymer in any solvent do not depend on the nature of the solvent, as far as the solvent has no influence on the rotation of the chain segments. In this case K_Θ is a constant. The evaluation of K_Θ from $[\eta]$–M data by application of the classical Burchard–Stockmayer–Fixman (BSF) theory often results in different values, with dependence on solvent power and, with mixed solvents, on solvent composition. This is mainly due to the non-linearity of the relationship, especially with high molar mass polymers in good solvents. Better results are obtained by non-linear graphical treatment of the BSF plot, or by application of a modified equation proposed by Tanaka, which takes into account the general $\alpha^5 \sim z$ relationship between molecular expansion factors and the excluded volume parameter z. Plots of $([\eta]/M^{0.5})^{5/3}$ *versus* $M^{0.5}$ show linearity over nearly the entire range of molar mass studied and evaluation of unperturbed dimensions results in a quasi unique value of K_Θ for a given polymer.

INTRODUCTION

Besides light scattering measurements on polymers in solution, the investigation of their rheological properties remains an easily managed and efficient method of polymer characterization. With the Mark–Houwink (MH) relation $[\eta] = KM^a$, which holds remarkably well for most polymers in most solvents over a rather broad range of molar mass, the characteristic parameters a and K are obtained from intrinsic viscosity data. These parameters depend on the polymer, solvent and temperature, and, for a given polymer, the better the solvent the higher the value of the exponent a and the lower the value of the constant K. For chain polymers the exponent a is in the range of 0.8 in a good solvent to 0.5 in a θ solvent, where $K = K_\Theta$ describes the unperturbed dimensions of the chain. In solutions of non-θ conditions the chain molecule is expanded due to the excluded volume effect and the unperturbed dimensions are obtained from $[\eta]$–M data by application of the well-known Burchard–Stockmayer–Fixman (BSF)[1] equation.

In general the unperturbed dimensions parameter K_Θ should be a constant for a given polymer in any solvent[2–4], as far as there is no strong influence on the relative energies of rotational isomeric states of the chain segments. While this is true in many cases, especially when data are obtained for non-polar polymers in non-polar solvents, in the case of polar polymers and polar solvents this quantity can vary considerably.

However, in order to have measurable effects, one has to deal with polymers having either polar side groups or side groups able to form hydrogen bonds easily.

Nevertheless, as known from the literature, in many cases not a single K_Θ is obtained, when it is derived from diverse binary and ternary solutions of the same polymer. In our opinion in a large number of these cases the evaluation of K_Θ according to the BSF relation, which is usually done by linear extrapolation to $M = 0$ in a plot of $[\eta]/M^{0.5}$ *versus* $M^{0.5}$, is performed incorrectly, as in good solvents and even in poor solvents in the range of high molar masses experimental data do not coincide with the linearity of the formula. Although the curvature of the BSF plot is well known and many efforts have been made to achieve relations of better linearity, this discrepancy often is not recognized and values of K_Θ are obtained, which show an apparent dependency on the solvent and, when ternary polymer solutions are investigated, on solvent composition.

Furthermore, the unperturbed dimensions are predicted to depend on temperature due to the thermodynamic equilibrium ratio of *trans* to *gauche* conformations of the chain segments. For example, the value of $K_\Theta = 0.088$ ml g^{-1} for polystyrene in the θ solvent cyclohexane (34.5°C) is due to a higher rate of *trans* conformation. Although this is generally true, other experimental results could mainly be related to the kind of evaluation than to the influence of temperature.

In this paper we discuss the evaluation of K_Θ with experimental data from binary polymer–solvent systems and from ternary polymer1–polymer2–solvent systems, obtained in our laboratory, and with the results of

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Table 1 Polystyrene samples

Sample	M_w $(\times 10^6 \, g \, mol^{-1})$	M_w/M_n
PS1	0.152	1.05
PS2	0.233	<1.06
PS3	0.400	<1.06
PS4	0.612	<1.10
PS5	0.860	<1.10
PS6	0.950	<1.10
PS7	1.46	<1.10
PS8	1.86	1.12
PS9	2.95	1.06
PS10	4.34	1.06
PS11	5.50	1.10
PS12	6.50	1.12
PS13	8.50	1.20
PS14	9.35	<1.20
PS15	10.30	1.25

other laboratories, given in recent papers. Besides the application of linear and non-linear extrapolation according to BSF the unperturbed dimensions are determined through a modified $[\eta]-M$ relationship suggested by Tanaka. Further account is taken of the preconditions of these theories and of theories which allow for the dependence of the interaction parameter B on molar mass.

EXPERIMENTAL

The viscometric measurements were performed with a Couette-type rotational viscometer (CV100, Haake, Germany) at 20°C. The measurements were performed on polystyrene standards (*Table 1*), purchased from Pressure Chemical Company, USA (PS1–PS8) and from Polymer Laboratories Ltd, UK (PS9–PS15) in p.a. grade toluene and pure (>99%) *trans*-decalin, and in mixtures of oligostyrene (commercial product donated by BASF, Germany), $M_w = 1300 \, g \, mol^{-1}$, or poly(methylvinylether) (PMVE, commercial product by GAF-Corp., Germany), $M_w = 130000 \, g \, mol^{-1}$, in toluene. The commercial samples contained $\sim 50 \, wt\%$ polymer in toluene. Newtonian fluid properties were shown for oligostyrene/toluene compositions up to 52 wt% of the commercial sample and for PMVE/toluene compositions up to 21 wt% of the commercial sample. The viscometric measurements were performed on dilute solutions with a maximum polymer concentration of about double overlap concentration c^*, defined by $c^* = 1/[\eta]$, and the obtained reduced viscosity numbers were extrapolated to zero concentration and zero shear rate. *Table 2* lists the solvents and their abbreviations.

THEORY

Experimental evidence shows that for macromolecules with a sufficient degree of coiling (i.e. for a high enough number of segments, typically $M > 10^4$) the value of the friction coefficient ζ is such that the coil is hydrodynamically in the limiting non-draining state[5]. In this state the hydrodynamic properties no longer depend on ζ and the properties of polymer solutions are fully described by the two-parameter theories. The two parameters are the unperturbed dimensions of the coil,

$\langle R^2 \rangle_\Theta/M$, and the excluded volume parameter z, defined as:

$$z = (3/2\pi)^{1.5} B A^{-3} M^{0.5} \tag{1}$$

where $\langle R^2 \rangle_\Theta$ is the mean-square end-to-end distance of the unperturbed coil, B is the long-range interaction parameter, correlated to the polymer–solvent interactions and A is the short-range interaction parameter related to the unperturbed dimensions through $A^2 = \langle R^2 \rangle_\Theta/M$. The short-range interaction parameter provides information about the local conformation of the polymer chain due to steric and/or thermodynamic interaction with the solvent, and the long-range interaction parameter describes the influence of the excluded volume effect, which is basically due to the thermodynamic interaction of the polymer–solvent pair.

From intrinsic viscosity measurements in a θ solvent, where the intrinsic viscosity is proportional to the square root of M, the unperturbed dimensions can be directly evaluated by application of the Mark–Houwink equation in the form of $[\eta] = K_\Theta M^{0.5}$, where K_Θ is related to the unperturbed dimensions by $K_\Theta = \Phi_0 A^3$ and $\Phi_0 = 2.862 \times 10^{23} \, mol^{-1}$ is the universal Flory constant for chain polymers in θ solvents in the non-draining limit. In any better solvent the expansion of the polymer coil has to be taken into account by introducing the viscosity expansion factor, defined by Flory as $\alpha_\eta^3 = [\eta]/[\eta]_\Theta$. For flexible chains α_η^3 is a function only of the excluded volume parameter z and the first perturbation calculations of Kurata and Yamakawa[6] yield the approximate result $\alpha_\eta^3 = 1 + 1.55z$ in the limit of large excluded volume. Now, inserting the expansion factor, its relation to z, and equation (1) into the MH equation for the θ state the well-known equation:

$$[\eta]/M^{0.5} = K_\Theta + 0.51\Phi_0 B M^{0.5} \tag{2}$$

is developed, which has been proposed first by Burchard[1] and by Stockmayer and Fixman[7]. Plotting $[\eta]/M^{0.5}$ as a function of $M^{0.5}$ the points in the high molar mass region should approach a line of constant slope and its extrapolation to zero molar mass gives the value of K_Θ. On the other hand, the slope of this line is a measure of long-distance interactions and is directly proportional to B. Up to now this simple procedure has been favoured by many experimentalists, but often the limitations of this method are not considered or deviation from the predicted linearity is not recognized. While the procedure works reasonably well for rather poor solvents, for good solvents, and even for high molar mass polymers in solutions of medium solvent power, a slightly curved dependence is obtained. The scatter of experimental data points may obscure this curvature and extrapolation may become ambiguous. Performing the graphical extrapolation to zero molar mass by a straight line, the values of its intercept and slope depend on the

Table 2 List of solvents

Designation	Solvent
TOL	Toluene
DEP	Diethylphthalate
DEC	*trans*-Decalin
Oligo 10	10 wt% oligostyrene in toluene
Oligo 30	30 wt% oligostyrene in toluene
PMVE 4	4 wt% poly(methylvinylether) in toluene
PMVE 17	17 wt% poly(methylvinylether) in toluene

selected range of molar mass and, consequently, their interpretation is rather meaningless.

However, if one considers the MH equation as a good representation of the experiment and plots $[\eta]/M^{0.5}$ versus $M^{0.5}$ as calculated from the MH equation, the curvature within the valid range of molar mass becomes obvious (Figures 1 and 2). The degree of curvature is considerably dependent on the polymer–solvent pair and rises with increasing solvent power. For this reason, especially from investigations of ternary polymer solutions, where the thermodynamic quality of the solution varies with solvent composition, an apparent dependency of K_Θ on solvent power is obtained, when possible curvature is neglected. Different results would be obtained, when the extrapolation to vanishing molar mass is performed by following the curvature. For polystyrene in various solvents (given in Table 2) and for polyisobutylene in some solvents[8] values of MH parameters and of K_Θ, evaluated through different procedures, are given in Tables 3 and 4, respectively. The three digits after the decimal point, given for the numerical value of the exponent a, do not represent the experimental
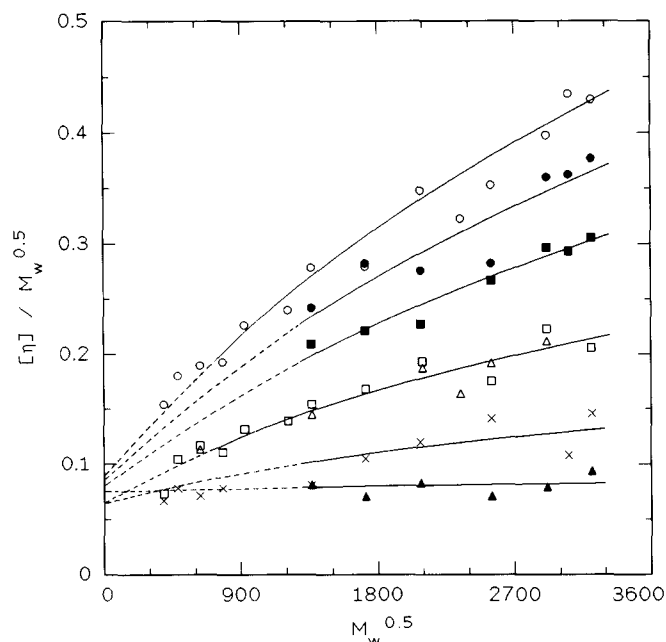
accuracy but they are necessary for the relation to be valid over a very large range of molar mass.

As the procedure of non-linear extrapolation to zero molar mass by following the downward curvature is quite uncertain, many efforts have been made to improve the linearity of the BSF plot. One of the first useful modifications of the BSF equation was achieved by Berry[9], who suggested plotting $([\eta]/M^{0.5})^{0.5}$ versus $M/[\eta]$ according to the semi-empirical relationship:

$$([\eta]/M^{0.5})^{0.5} = K_\Theta^{0.5} + 0.42(\Phi_0 A)^{1.5}B(M/[\eta]) \qquad (3)$$

Although good results are obtained by this method, it may be noted that experimental error in $[\eta]$ both influences the left-hand term $([\eta]/M^{0.5})^{0.5}$ and the right-hand term $M/[\eta]$ of this equation. As far as the values of $[\eta]$ are relatively small in comparison to M ($[\eta]/M \approx 10^{-4}$), i.e. in poor solvents, experimental error in $[\eta]$ does not matter so much in a graphical treatment. In good solvents, however, where the intrinsic viscosity numbers and their absolute experimental errors grow larger, the evaluation of K_Θ according to equation (3) may become uncertain.

A new point of view in the discussion of the

Figure 1 Classical BSF plot for polystyrene at 20°C in toluene (O), Oligo 10 (●), Oligo 30 (■), PMVE 4 (□), PMVE 17 (×), DEP (△) and trans-decalin (▲). The solid-lines are calculated using the MH parameters, the dashed lines show non-linear graphical extrapolation to vanishing molar mass
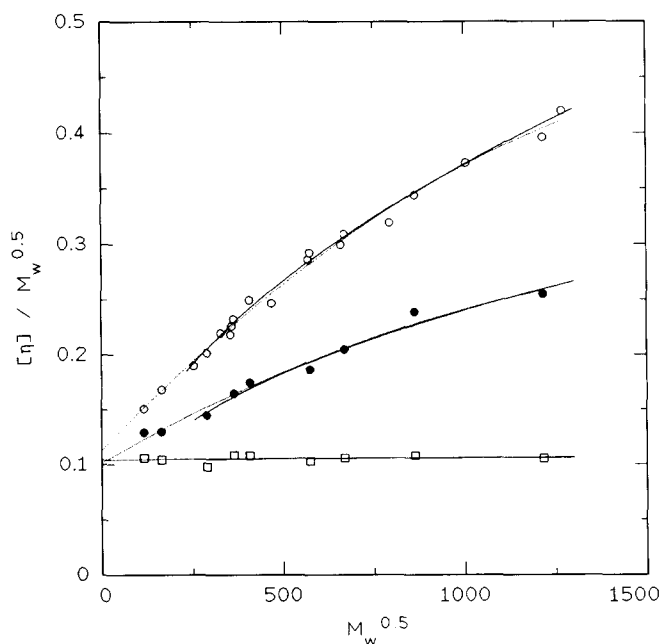

Figure 2 Classical BSF plot for polyisobutylene[8] at 25°C in cyclohexane (O), n-heptane (●) and benzene (□). The solid lines are calculated using the MH parameters, the dotted lines are second-order polynomial fits

Table 3 Mark–Houwink parameters and K_Θ for polystyrene in different solvents at 20°C

			K_Θ (ml g^{-1})			
Solvent	a	K (10^{-3} ml g^{-1})	BSF$_{linear}$	BSF$_{graphical}$	BER	TAN
TOL	0.769	5.57	0.127	0.090	0.079	0.081
DEP	0.706	7.59	0.088	0.082	0.078	0.075
DEC	0.523	56.8	0.067	0.077	0.077	0.066
Oligo 10	0.760	5.48	0.139	0.085	0.189	0.074
Oligo 30	0.747	5.61	0.125	0.080	0.081	0.085
PMVE 4	0.714	6.75	0.083	0.065	0.062	0.071
PMVE 17	0.647	12.27	0.086	0.066	0.097	0.077

K_Θ is determined according to Burchard–Stockmayer–Fixman (BSF), Berry (BER) and Tanaka (TAN). The range of molar mass is $1.52 \times 10^5 \leqslant M_w \leqslant 10.3 \times 10^6$ g mol^{-1} for TOL and PMVE 4 and $1 \times 10^6 < M_w \leqslant 10.3 \times 10^6$ g mol^{-1} for the other solvents

Table 4 Mark–Houwink parameters and K_Θ for polyisobutylene in different solvents[8] at 25°C

Solvent	a	K $(\times 10^{-3} \, \text{ml g}^{-1})$	K_Θ (ml g^{-1})			
			BSF$_{\text{linear}}$	BSF$_{\text{non-linear}}$	BER	TAN
Cyclohexane	0.740	13.5	0.143	0.113	0.088	0.111
n-Heptane	0.697	15.8	0.116	0.102	0.097	0.106
Benzene	0.504	100	0.104	0.104	0.104	0.104

K_Θ is determined according to Burchard–Stockmayer–Fixman (BSF), Berry (BER) and Tanaka (TAN). $6.4 \times 10^4 \leqslant M_w \leqslant 1.48 \times 10^6 \, \text{g mol}^{-1}$
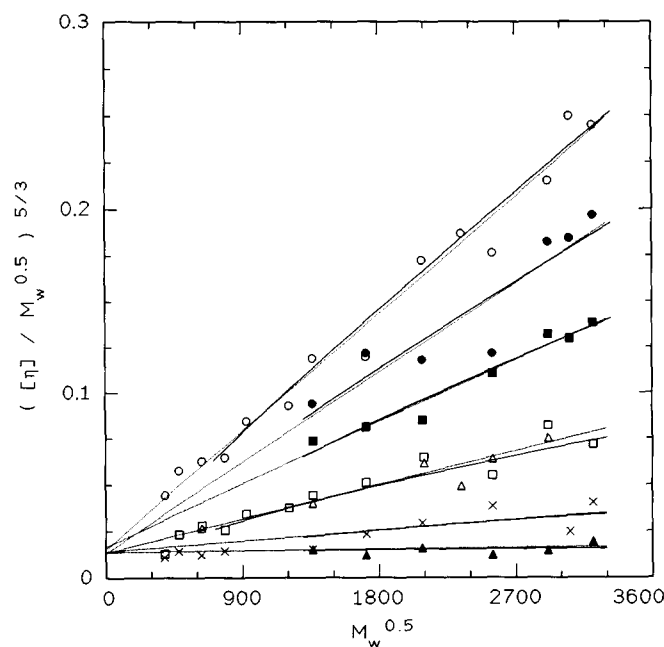

Figure 3 Plot of $([\eta]/M_w^{0.5})^{5/3}$ *versus* $M_w^{0.5}$ according to Tanaka[12] for polystyrene at 20°C in toluene (O), Oligo 10 (●), Oligo 30 (■), PMVE 4 (□), PMVE 17 (×), DEP (△) and *trans*-decalin (▲). The solid lines are calculated by using the MH parameters, the dotted lines are linear least squares fits
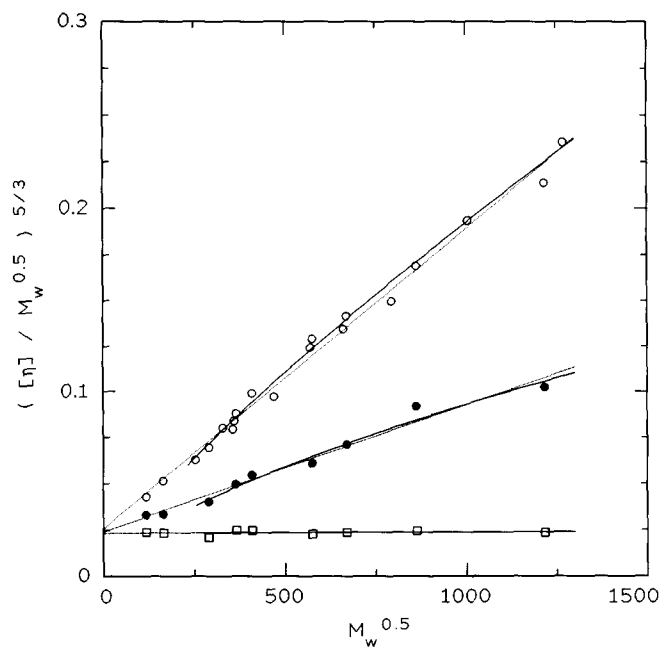

Figure 4 Plot of $([\eta]/M_w^{0.5})^{5/3}$ *versus* $M_w^{0.5}$ according to Tanaka[12] for polyisobutylene in cyclohexane (O), n-heptane (●) and benzene (□)[8]. The solid lines are calculated using the MH parameters, the dotted lines are linear least squares fits

determination of unperturbed dimensions arose with the experience[10] that any expansion factor retains the same limiting functional form in the limit of large excluded volume, written as $\lim_{z \to \infty} (\alpha^5/z) = \text{constant}$. It followed that the presumption of the BSF theory, predicting the viscosity expansion factor α_η to be asymptotically proportional to $z^{1/3}$ in the region of large excluded volumes, was incorrect[11]. On the basis of these statements Tanaka[12] showed that simple Padé approximants give good results over the entire range of positive z for expansion factors of viscosity and friction coefficient radii. Furthermore, good fits to experimental data were obtained through the general relation $\alpha^5 = 1 + (\text{constant} \times z)$, so the Tanaka modification of the BSF equation results in:

$$([\eta]/M^{0.5})^{5/3} = K_\Theta^{5/3} + 0.627\Phi_0^{5/3}A^2 BM^{0.5} \qquad (4)$$

replacing $\alpha_\eta^3 = 1 + 1.55z$ by $\alpha_\eta^5 = 1 + 1.90z$. Evaluation of the unperturbed dimensions parameter K_Θ and of the interaction parameter B according to equation (4) is performed by plotting $([\eta]/M^{0.5})^{5/3}$ as a function of $M^{0.5}$ (*Figures 3* and *4*). By linear extrapolation to vanishing molar mass B is obtained from the slope and the ordinate intercept directly gives $K_\Theta^{5/3}$. In comparison to the BSF plot the linearity of experimental data is proposed to hold over the entire range of molar mass in a plot

according to the Tanaka relation, even in very good solvents, and determination of K_Θ should be more reliable. Results of this kind of evaluation are also given in *Tables 3* and *4*.

While in all the theories mentioned above and many other modifications of the BSF theory the interaction parameter B is taken to be independent of molar mass, later studies[13,14] allow for the dependence of B on molar mass. Generally B is related to the Flory interaction parameter χ, which is considered to be independent of molar mass, through $B = [2\bar{v}^2/(N_A V)](0.5 - \chi)$, where $\bar{v}$ is the partial specific volume of the polymer, V is the molar volume of the solvent and N_A is Avogadro's number. Wolf[13], however, who studied the influence of M on the second virial coefficient A_2 through the interaction parameter χ, considered χ to be dependent on molar mass, originating from two different interactions between polymer segments, one intermolecular and the other intramolecular in nature, when $A_2 \neq 0$. As the viscometric interaction parameter is related to the second virial coefficient through the expression $B = 2A_2/N_A$, consequently B is a function of M, as far as A_2 is a function of M.

Replacing the parameter B by a molar-mass-dependent second virial coefficient, $A_{2,M}$, Gavara, Campos and Figueruelo (GCF)[14] semi-empirically developed a
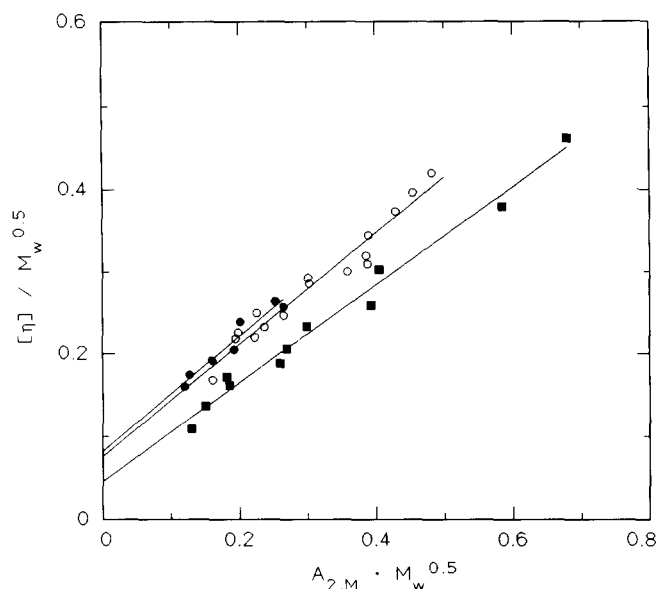
Figure 5 Modified BSF plot[14] considering the molar mass dependence of B through the second virial coefficient $A_{2,M}$ for polystyrene in toluene[17] (■) and polyisobutylene in cyclohexane (○) and n-heptane[8] (●)

modified form of the BSF equation, written as:

$$[\eta]/M^{0.5} = K_\Theta + 0.52 A_{2,M} M^{0.5} \qquad (5)$$

which is almost equal to an earlier equation suggested by Krigbaum[15], who, however, considered A_2 to be independent of molar mass. According to equation (5), values of K_Θ are determined from the ordinate intercept in a plot of $[\eta]/M^{0.5}$ versus $A_{2,M}M^{0.5}$ (*Figure 5*); the value of 0.52 for the constant factor on the right-hand side of the equation has been obtained experimentally from such diagrams. Evaluating the unperturbed dimensions of polymers in several binary and ternary (solvent1–solvent2–polymer) solutions with the use of equation (5), Gavara *et al.* obtained a unique value of K_Θ for a given polymer. From their later studies on other excluded volume theories[16], they draw the conclusion that introducing the molar mass dependence of A_2 minimizes the dispersion of points in plots of any of these theories. Furthermore, equation (5) is considered to give the best results, although its experimental validity is limited by $\alpha_\eta \leqslant 1.6$; above this value deviations from linearity are observed. Therefore even equation (5) fails when measurements are performed on high molar mass polymers in solutions of medium solvent power and in good solvents.

If we now account for the dependency of the interaction parameter B on molar mass, replace B by the second virial coefficient $A_{2,M}$, and plot $([\eta]/M^{0.5})^{5/3}$ versus $A_{2,M}M^{0.5}$, we obtain a correlation which takes care both of the α_η^5 relation and of the influence of molar mass on polymer–solvent interactions. An example, with experimental data from references 8 and 17, is given in *Figure 6*.

RESULTS AND DISCUSSION

We now evaluate K_Θ of polystyrene using some thermodynamically different binary and ternary solutions, by applying the above theories. For this, we take toluene as a very good solvent, *trans*-decalin as a near-θ solvent and diethylphthalate as in between. As ternary

solvent1–solvent2–polymer systems have already been investigated by other authors[14,15] further measurements were performed on polymer1–polymer2–solvent systems, where polymer1 is represented by the investigated polymer polystyrene and the polymer2–solvent pair, with constant molar mass of polymer2, is considered as the solvent of polymer1. With increasing weight fraction of polymer2 in toluene the average amount of solvent power declines and a variation in solvent quality is achieved (see MH parameters in *Table 3*).

Figure 1 is a classical BSF plot for polystyrene in the solvents described in *Table 2*, and *Figure 2* is the same plot for polyisobutylene in different single solvents with data taken from reference 8. Although the points referring to experimental data are of adequate linearity especially in the high molar mass region ($M_w > 10^6$ g mol^{-1}), and linear extrapolation to zero molar mass seems reasonable, the lines calculated from the respective MH relations are not in agreement with this linearity. Especially in the good polymer systems polystyrene/TOL, polystyrene/Oligo, polystyrene/PMVE 4 and polyisobutylene/cyclohexane a downward curvature of this line with increasing molar mass is obvious, and is stronger in the low molar mass region. If in the determination of K_Θ this curvature is neglected at all, or if, according to the BSF theory, the linear extrapolation to $M = 0$ is done from the region of high molar masses, values of K_Θ are obtained, which show significant dependency on solvent power and on the chosen range of molar mass. While these values are larger than those obtained from θ solvents (polystyrene/DEC, polyisobutylene/benzene), a unique value of K_Θ (within experimental error) is determined by non-linear extrapolation to $M = 0$, on following the curvature. The dashed lines in *Figure 1* show the graphical non-linear extrapolation in the BSF plot of polystyrene solutions and the dotted lines in *Figure 2* are second-order polynomial fits to the experimental data. The results of the linear and non-linear extrapolation in the BSF plot are listed in *Table 3* for solutions of polystyrene and in *Table 4* for solutions of polyisobutylene.

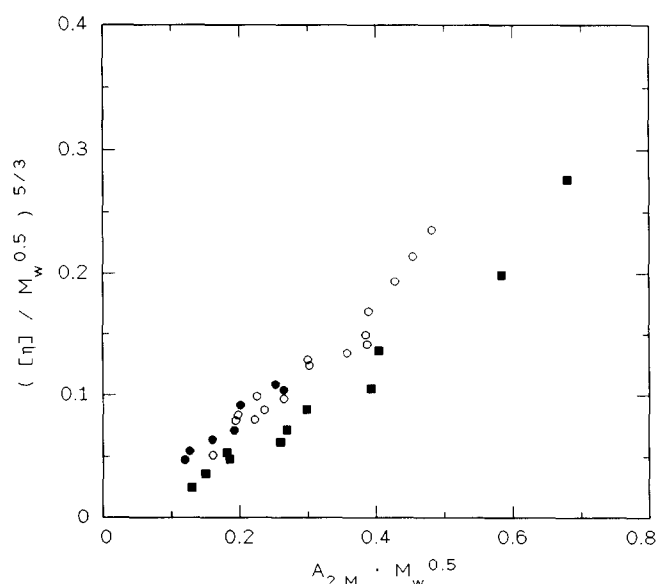When the same sets of $[\eta]$–M data are plotted

Figure 6 Modified BSF plot considering both the molar mass dependence of B and the $\alpha^5 \sim z$ relation for polystyrene in toluene[17] (■) and polyisobutylene in cyclohexane (○) and n-heptane[8] (●)
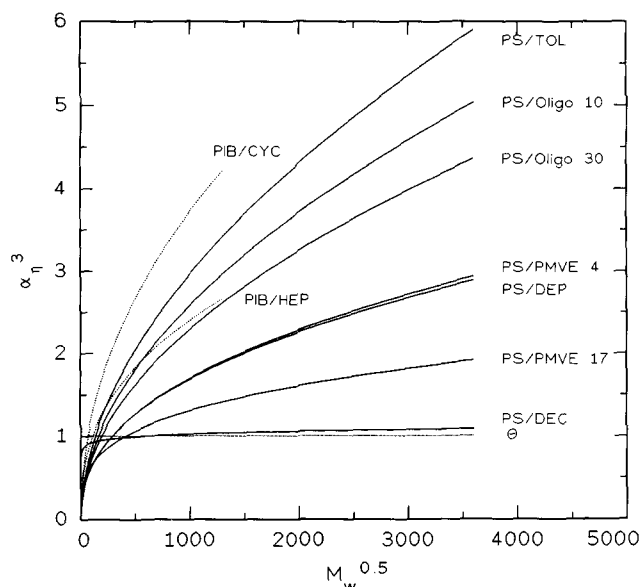
Figure 7 Replacement of the BSF plot by a relationship between the viscosity expansion factor α_η^3 and $M^{0.5}$. The lines are calculated using the MH parameters through equation (6), even in the low molar mass region where the MH relations are no longer valid

(*Figures 3* and *4*) according to equation (4), in the following denoted as Tanaka plots, points of experimental data and calculated curves appear to show excellent linearity over the entire range of molar mass. This linearity holds remarkably well even in good solutions and the evaluation of K_Θ results in values which may be considered as unique in the range of experimental error (*Tables 3* and *4*).

Difficulties in the evaluation occurred with the data set of polystyrene in PMVE 17, because in the low molar mass region intrinsic viscosity numbers are as large as in the unperturbed state and in the range of higher molar mass the scatter of points is relatively large.

In order to discuss K_Θ evaluation by application of the BSF plot and the Tanaka plot these plots may now be replaced by quasi equivalent plots[12] of the viscosity expansion factor *versus* $M^{0.5}$, remembering that $\alpha_\eta^3 = f(z)$ in the BSF theory and $\alpha_\eta^5 = f(z)$ in the modification of Tanaka, and that $M^{0.5}$ is proportional to the excluded volume parameter z through equation (1). By analogy, a replacement of the BSF plot is given by a plot of α_η^3 *versus* $M^{0.5}$ (*Figure 7*) and the Tanaka plot is equivalent to a plot of α_η^5 *versus* $M^{0.5}$ (*Figure 8*). Mathematical expressions for these two relations are simply derived from the definition of the viscosity expansion factor, $\alpha_\eta^3 = [\eta]/[\eta]_\Theta$, by use of the general form of the MH equation as:

$$\alpha_\eta^3 = (K/K_\Theta)M^{(a-1)}M^{0.5} \qquad (6)$$

and with $\alpha_\eta^5 = (\alpha_\eta^3)^{5/3}$ as:

$$\alpha_\eta^5 = (K/K_\Theta)^{5/3}M^{(a-0.8)5/3}M^{0.5} \qquad (7)$$

The curves in the two diagrams, calculated with the MH parameters given in *Tables 3* and *4*, demonstrate these dependencies, not only in the valid range of molar mass, but down to $M = 0$. The calculations were performed with $K_{\Theta,PIB} = 0.104$ ml g^{-1} (from the θ system polyisobutylene/benzene) and with $K_{\Theta,PS} = 0.076$ ml g^{-1}, which has been measured and calculated by other authors[14,18] and which can be taken as an average value of our experimental results. In further analogy the

extrapolation of $[\eta]$–M properties from any non-θ polymer–solvent system to the unperturbed state, i.e. the determination of unperturbed dimensions, is equivalent to an extrapolation of the expansion factor to unity at vanishing molar mass. In the unperturbed state, i.e. in θ solvents, α is unity over the whole range of M by definition. From *Figures 7* and *8* it is seen that all curves start at the origin, followed by a strong curvature in the low molar mass region. With increasing molar mass the degree of curvature declines until a quasi linear relation is reached in the high molar mass region. Nevertheless, the slope does not really approach a limiting value, as is predicted by the excluded volume theory. In further contradiction to theory a linear extrapolation of the limiting slope in the α_η^3–$M^{0.5}$ plot, which represents the BSF theory, to $M = 0$ does not yield $\alpha = 1$, except for the polystyrene/DEC system, which is nearly under θ conditions. If the extrapolation is performed from the region where $\alpha_\eta^3 \approx 2.5$ (the BSF theory is valid only up to this limiting value), the resulting values of the ordinate intercept are in an adequate range about $\alpha = 1$. However, if the graphical extrapolation is performed from a region far below or above $\alpha_\eta^3 \approx 2.5$, the intercept, and in analogy the value of the unperturbed dimensions parameter, will be smaller or larger than the real value for the unperturbed state. As in practice it is not possible to calculate the viscosity expansion factor at first, in application of the BSF plot the quality of the results depends on the chosen range of molar mass. Compared to the α_η^3–$M^{0.5}$ plot the linearity of the curves in the α_η^5–$M^{0.5}$ plot (*Figure 8*) is much better and the extrapolation to $\alpha = 1$ at vanishing molar mass can be performed over a wide range of molar mass, even from polymer–solvent systems which are strongly influenced by the excluded volume effect (polystyrene/TOL, polystyrene/Oligo).

As the curves in *Figures 7* and *8* are drawn from the origin, they cut the $\alpha = 1$ line at a special value of molar mass which, for a given polymer, increases with decreasing solvent power. This value may be correlated to the critical molar mass where the slope in the MH
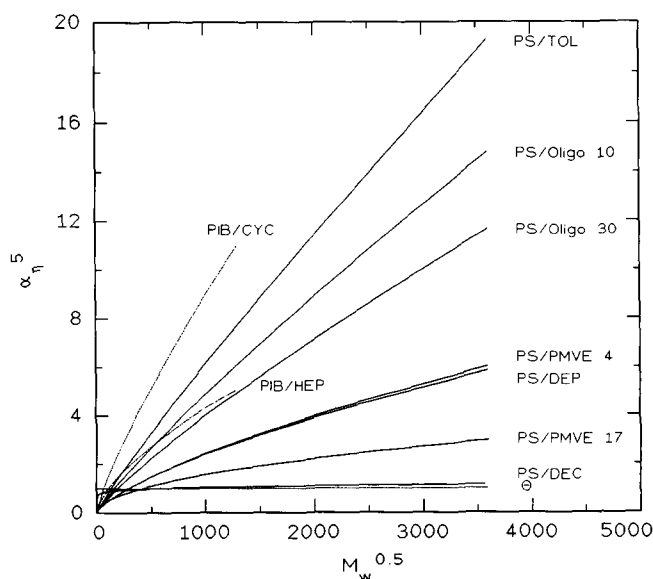

Figure 8 Replacement of the Tanaka plot by a relationship between the viscosity expansion factor α_η^5 and $M^{0.5}$. The lines are calculated using the MH parameters through equation (7), even in the low molar mass region where the MH relations are no longer valid

diagrams changes from 0.5 to the typical value of the polymer–solvent system, denoted by the MH exponent a. In the polystyrene/PMVE 17 system the critical molar mass is $\sim 5 \times 10^5\,\mathrm{g\,mol^{-1}}$ and polymer properties are as in the unperturbed state below this value, and K_Θ evaluation has to be performed with data from the high molar mass region only. In practice, however, the scatter of points may obscure the break in the $[\eta]$–M relation and the resulting unperturbed dimensions are too small when the low molar mass data are included in the evaluation. On the other hand, the evaluation yields a larger K_Θ when only high molar mass data are available, and the scatter of points may obscure the real slope in the diagram. For these reasons it is essential to measure over a broad range of molar mass and to ensure that the evaluation is performed only with data above the critical molar mass.

In order to discuss K_Θ evaluation by application of equation (5), which accounts for the molar mass dependency of the polymer–solvent interactions through $A_{2,M}$, data were taken from Fetters et al.[8] for polyisobutylene solutions and from Kniewske and Kulicke[17] for polystyrene in toluene. As predicted by Gavara et al. the dispersion of points is minimized when $[\eta]/M^{0.5}$ is plotted versus $A_{2,M}M^{0.5}$ (Figure 5) and a good linearity is achieved. However, the obtained values of K_Θ are much smaller in comparison to the values (Tables 3 and 4) evaluated by the methods mentioned above: $K_\Theta = 0.046\,\mathrm{ml\,g^{-1}}$ for polystyrene in toluene and $K_\Theta = 0.080\,\mathrm{ml\,g^{-1}}$ as a mean value for polyisobutylene. In their comparative study Gavara et al.[16] discussed the deviations in K_Θ values obtained from different modified excluded volume theories, but they did not compare these results to the values which would be derived by application of the original equations. Their figures, however, show that there are differences in the results and that sometimes the original plot gives more reliable values than the modified one. Although the theoretical background of the GCF relation, equation (5), is widely accepted, its application on the evaluation of unperturbed dimensions seems not to be applicable in the suggested form.

If we finally introduce the α^5 relation in the GCF theory (Figure 6), an upward curvature in the plot occurs and the K_Θ evaluation appears to be quite difficult and meaningless. The obtained results may be the same as from Figure 5, but more erroneous in practical determination.

CONCLUSIONS

From the above results the following conclusions can be drawn concerning the evaluation of unperturbed dimensions from $[\eta]$–M data. On the one hand, classical treatment according to the BSF theory is quite adequate if poor solvents or solutions of medium solvent power

are used. Otherwise non-linear extrapolation in the BSF plot has to be performed, preferably with data calculated through the MH relationship. When the dispersion of experimental data points is not too large, remarkably good results are also obtained by application of the Berry equation. The evaluation of K_Θ from solutions with a strong influence of the excluded volume effect should be performed using the Tanaka plot, which shows good linearity over nearly the entire range of molar mass. Excellent graphical linearity is also obtained when account is taken of the molar mass dependence of the polymer–solvent interactions, as proposed by Gavara et al. but the resulting K_Θ values differ from those derived through the above-mentioned relations. In general, intrinsic viscosity data should be determined over a broad range of molar mass to improve the quality of the evaluation, and in order to obtain reliable results the evaluation should be performed by more than one method.

As far as the rotational isomeric states of the chain segments are not affected by the solvent or through temperature, the unperturbed dimensions of a given polymer are expected to be constant. In these cases the determined values, obtained by variation of solvent or temperature, should coincide within the range of experimental error. Nevertheless it should be kept in mind that in principle there may be a dependence of K_Θ on solvent and temperature. This effect will also be seen in the MH relationship.

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