Limitations of graphical procedures based on excluded-volume theories for the determination of K_θ

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The $[\eta]$–M relations of some commonly used two-parameter excluded-volume theories have been considered in regard to estimating K_θ, a measure of unperturbed dimensions of polymers. Limitations of these theories have been demonstrated using $[\eta]$–M data of two substituted acrylamide polymers, poly(*N*-phenyl acrylamide) (PNPA) and poly(*N*-(*p*-methyl)phenyl acrylamide) (PNPMPA), which range in their ν values from flexible to semi-rigid chain character. The analysis shows that the theories fail to accommodate any such set of $[\eta]$–M data that leads to ν values larger than its prescribed limit in the corresponding theory. For the Flory–Fox–Schaefgen and Domb–Barrett theories $\nu_{\max}$ came out to be 0.80; and for the Kurata–Stockmayer–Roig, Burchard–Stockmayer–Fixman and Inagaki–Ptitsyn theories it extended to unity. As a consequence of the failure of these theories, two more equations due to first-order perturbation and Bueche–James theories were invoked with a view to extending the scope of this analysis. The upper limit of ν was thus extended to 1.25 and 2.00, respectively. These theories were found to be of general applicability. The values of K_θ estimated by appropriate methods were 4.65×10^{-4} and 8.5×10^{-4} dl mol$^{1/2}$ g$^{-3/2}$ for PNPA and PNPMPA, respectively.

(Keywords: excluded volume; unperturbed dimensions; random flight model; intrinsic viscosity; expansion parameter; substituted acrylamide polymers)

INTRODUCTION

In the study of solution properties of macromolecules it is of considerable interest to determine their molecular dimensions in the unperturbed state, i.e. when both the attractive and the repulsive forces acting on the polymer chains counterbalance each other. The unperturbed dimensions, which represent short-range interactions of polymer chains, provide information regarding the structure and hydrodynamic behaviour of the chains. They can be obtained directly by estimating the unperturbed mean-square radius of gyration $\langle S^2 \rangle_0$ from light scattering measurements in a theta solvent. However, a theta solvent is not readily available in all cases. Also, in crystalline polymers the solvent power required to overcome the inter- and intramolecular interactions often results in a large value of the expansion parameter, α. Therefore, in many cases certain graphical procedures, based on two-parameter excluded-volume theories, are used to determine K_θ, which is a direct measure of unperturbed dimensions of polymers, making use of their intrinsic viscosity ($[\eta]$) and molecular weight (M) data.

Experimental $[\eta]$–M data of certain polymers, like *trans*-1,4-polyisoprene[1], have been found to adhere to nearly all the two-parameter theories. But it is revealed from the literature[2–8] that many synthetic and natural polymers obey different excluded-volume theories in good solvents. Thus the data of amylose benzoate[4], polybut-1-ene[5], cellulose triacetate[6], cellulose trinitrate[6], amylose acetate[7] and amylose propionate[8] show that their behaviour is quite different in good solvents, and cannot be explained by a single theory of excluded volume. Perhaps for this reason a note of caution was recommended by Berry and Fox[9], who stressed the need to make a proper choice of the theories for the treatment of experimental data. The same fact was pointed out by Flory[10], i.e. that if these theories are applied indiscriminately, it may appear that a particular theory is applicable but the conclusions drawn could be quite contrary to the normal behaviour of the polymer molecule in solution. One of the objectives of this communication, therefore, was to test the validity and demonstrate the practical limitations of some commonly used two-parameter theories by $[\eta]$–M data of two substituted acrylamide polymers[11] that range in their ν values from flexible to semi-rigid chain character in different solvents.

The fact that $[\eta]$–M data of polymers are intimately related through the Mark–Houwink–Kuhn–Sakurada (MHKS) relationship, and give rise to distinct values of the constant ν under a set of experimental conditions, helped in searching for at least one of the criteria for testing the validity of any theory. It was conceived that

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the excluded-volume theories making use of these data should also be bound by the respective limits of v prescribed by every theory. Thus the other objectives of this communication were: (i) to investigate the theoretical limits of v for some commonly used excluded-volume theories; (ii) in consequence of the failure of these theories, to invoke equations with extended limits of v for general applicability; (iii) after a suitable test, to make a proper choice of theories that successfully take into account the excluded-volume effect operative in the solvent–polymer systems under consideration; and (iv) with the help of the successful theory, to estimate K_θ, for the substituted acrylamide polymers.

THEORY

According to Fox and Flory[12], $[\eta]$ is given by the relation:

$$[\eta]=[\eta]_\theta\alpha_\eta^3 \qquad (1)$$

For flexible polymer chains of ordinary molecular weight, $[\eta]$ at the theta temperature is given by the relation:

$$[\eta]_\theta=K_\theta M^{1/2} \qquad (2)$$

with

$$K_\theta=\Phi_0(\langle R^2\rangle_0/M)^{3/2} \qquad (3)$$

where K_θ is a measure of the unperturbed mean-square end-to-end distance $\langle R^2\rangle_0$, α_η is the linear expansion factor of molecular dimensions due to the excluded-volume effect, and Φ_0 ($=2.87\times10^{21}$) is Flory's universal constant.

Determination of K_θ in good solvents is followed by the application of graphical procedures based on two-parameter excluded-volume theories. The essence of all the theories is ultimately seen in the dependence pattern of the linear expansion parameter, α_η, upon the excluded-volume parameter, z. From equations (1), (2) and (3), α_η can be written as:

$$\begin{aligned}\alpha_\eta^3&=[\eta]/K_\theta M^{1/2}\\&=[\eta]/\{\Phi_0(\langle R^2\rangle_0/M)^{3/2}M^{1/2}\}\end{aligned} \qquad (4)$$

The excluded-volume parameter z is correlated with M as[2]:

$$z=(0.33\Phi_0 B/K_\theta)M^{1/2} \qquad (5)$$

In practice the two-parameter theories are combined with equations (4) and (5) to yield $[\eta]$–M relations, which in turn are extrapolated to zero molecular weight to estimate K_θ and the solvent–polymer interaction parameter, B. The foremost of the several graphical procedures is due to Flory, Fox and Schaefgen[12,13] (FFS), which correlates the expansion parameter α with z as follows:

$$\alpha^5-\alpha^3=2.6z \qquad (6)$$

This was translated into $[\eta]$–M form as:

$$\text{FFS}\qquad [\eta]^{2/3}/M^{1/3}=K_\theta^{2/3}+0.858K_\theta^{2/3}B\Phi_0(M/[\eta]) \qquad (7)$$

A plot of $[\eta]^{2/3}/M^{1/3}$ *versus* $M/[\eta]$ when extrapolated to $M=0$ will yield the values of K_θ and B.

In order to find the limitations of equation (7), two extreme approximations can be applied: (i) Under theta conditions the attractive and repulsive forces counterbalance each other, so that the expansion parameter α_η becomes unity, and the excluded-volume effect and hence the solvent–polymer interaction parameter become zero. Equation (7) then becomes:

$$[\eta]=K_\theta M^{1/2} \qquad (8)$$

(ii) On the other hand when the excluded-volume effect is very high (at large M and in very good solvents), equation (7) takes the form:

$$[\eta]^{2/3}/M^{1/3}=\text{constant}\times M/[\eta]$$

or

$$[\eta]=\text{constant}\times M^{4/5} \qquad (9)$$

A comparison of equations (8) and (9) with the MHKS relation ($[\eta]=KM^v$) shows that the lower and upper limits of v, as prescribed by the FFS relation, are 0.5 and 0.8, respectively, for linear flexible chains without a draining effect. A violation of this upper limit must then be interpreted as evidence for the draining effect, and consequently for high stiffness of chains. However, with the evolution of third-power-type equations for excluded volume due to Kurata, Stockmayer and Roig[14] (KSR), Burchard[15], Stockmayer and Fixman[16] (BSF) and Inagaki and Ptitsyn[2,17] (IP), the range of v was established as $0.5\leqslant v\leqslant 1$. The α *versus* z relations due to these theories read respectively as follows:

$$\alpha^3-\alpha=2.053z\{1+1/(3\alpha^2)\}^{-3/2} \qquad (10)$$

$$\alpha^3=1+1.55z \qquad (11)$$

$$4.67\alpha^2=3.67+(1+9.34z)^{2/3} \qquad (12)$$

The $[\eta]$–M translations of equations (10)–(12) can be written down as:

$$\text{KSR}\qquad [\eta]^{2/3}/M^{1/3}=K_\theta^{2/3}+0.363\Phi_0 B\{g(\alpha_\eta)M^{2/3}/[\eta]^{1/3}\} \qquad (13)$$

with

$$g(\alpha_\eta)=8\alpha_\eta^3/(3\alpha_\eta^2+1)^{3/2}$$

$$\text{BSF}\qquad [\eta]/M^{1/2}=K_\theta+0.51\Phi_0 BM^{1/2} \qquad (14)$$

$$\text{IP}\qquad [\eta]^{4/5}/M^{2/5}=0.786K_\theta^{4/5}+0.454K_\theta^{2/3}\Phi_0^{2/3}B^{2/3}M^{1/3} \qquad (15)$$

Besides these commonly used equations, the Domb–Barrett (DB) theory[18], which is free from the assumptions of the Gaussian distribution of the segments and the form of the binary clustered integral, seems to be adequate for flexible chains with $0.5\leqslant v\leqslant 0.8$. The DB equation and its $[\eta]$–M form as proposed by Patel *et al.*[19] are given in equations (16) and (17), respectively:

$$\alpha^{10}=1+\tfrac{20}{3}z+4\Pi z^2 \qquad (16)$$

$$\text{DB}\qquad ([\eta]/M^{1/2})^{10/3}=K_\theta^{10/3}+0.33\Phi_0 BK_\theta^{7/3}\{g(\alpha)M^{1/2}\} \qquad (17)$$

with

$$g(\alpha)=3.33+[11.1+12.56(\alpha^{10}-1)]^{1/2}$$

EXPERIMENTAL AND RESULTS

Synthesis and characterization of poly(N-phenyl acrylamide) (PNPA) and poly(N-(p-methyl)phenyl acrylamide) (PNPMPA) were reported earlier[11]. However, for convenience and comparison, the values of intrinsic viscosities

Table 1 Molecular-weight and viscosity (at 30°C) data of PNPA and PNPMPA fractions

				$[\eta]$ (dl g^{-1})			
Fraction	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-4}$	$\frac{\bar{M}_w}{\bar{M}_n}$	Dioxane	Dioxane: toluene (50:50)	Dioxane: toluene (30:70)	Acetone
PNPA-2	–	16.10	1.33	1.16	1.01	0.48	–
PNPA-3	–	15.00	–	1.14	0.81	0.48	–
PNPA-4	–	11.30	–	0.76	–	0.34	–
PNPA-6	–	9.70	1.22	0.71	0.54	0.33	–
PNPA-7	–	9.30	1.13	0.58	0.46	0.28	–
PNPMPA-2	7.40	–	1.85	1.24	–	–	1.00
PNPMPA-3	6.30	–	1.91	1.19	–	–	0.94
PNPMPA-4	5.70	–	2.88	1.10	–	–	0.91
PNPMPA-5	3.00	–	1.90	0.64	–	–	0.51

Table 2 Values of MHKS constants, K and ν, at 30°C for PNPA and PNPMPA in the indicated solvent systems

Polymer	Solvent system	ν	$K \times 10^6$ (dl g^{-1})
PNPA	Dioxane:toluene		
	100:00	1.16	1.08
	50:50	1.12	1.33
	30:70	1.00	3.16
PNPMPA	Dioxane	0.77	40.70
	Acetone	0.74	46.60

and molecular weights used in the present analysis are listed in *Table 1*. Additional data on the viscosities of some PNPA fractions in two mixtures of dioxane:toluene (v/v) also appear in the same table. The values of the MHKS constants, K and ν, for the systems under consideration are given in *Table 2*. The $[\eta]$–M data of these polymers were treated according to the graphical procedures suggested by the above two-parameter theories; the selected plots are shown in *Figures 1–4*.

Figures 1 and *2*, respectively, show KSR and BSF plots due to equations (13) and (14) for PNPMPA data in dioxane and acetone at 30°C. No specific solvent effect is observed on K_θ in either of the plots, as the extrapolated lines yield a common intercept on the ordinate. However, as seen in *Figure 3*, PNPMPA data fails to obey DB theory as the extrapolated lines intercept the ordinate at negative values.

Data on the number-average molecular weight and intrinsic viscosity of PNPA fractions in dioxane and dioxane–toluene mixtures at 30°C according to the IP equation are shown in *Figure 4*. It is interesting to note that the theory shows outright failure for the data in 100:0 and 50:50 dioxane:toluene mixtures. However, the data of the 30:70 dioxane:toluene mixture show partial compliance in the sense that the extrapolation of the line to $M=0$, unlike the other two lines, leads to a positive intercept; but the magnitude of K_θ comes out to be less than that derived from other methods (see *Table 4*).

DISCUSSION

In order to understand the cause of the failure of IP theory in the case of PNPA and DB theory in the case of PNPMPA, it is necessary to look at the limits of ν prescribed by different excluded-volume theories. As illustrated for FFS through equations (8) and (9), the

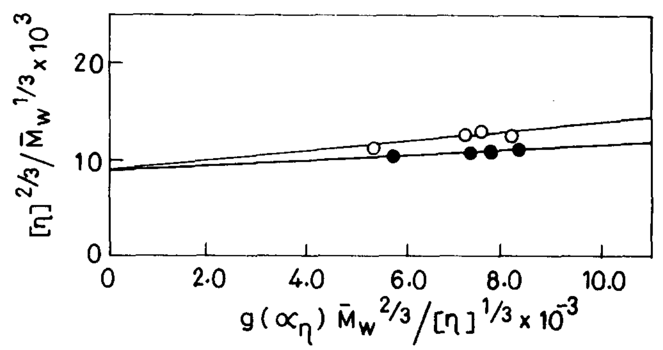

Figure 1 KSR plot of $[\eta]^{2/3}/\bar{M}_w^{1/2}$ *versus* $g(\alpha_\eta)\bar{M}_w^{2/3}/[\eta]^{1/3}$ for PNPMPA data in dioxane (○) and in acetone (●) at 30°C according to equation (13)

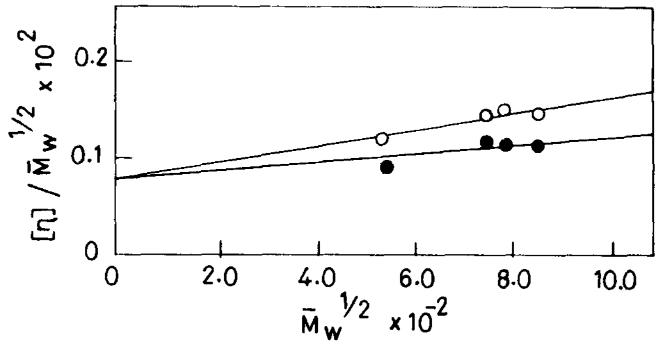

Figure 2 BSF plot of $[\eta]/\bar{M}_w^{1/2}$ *versus* $\bar{M}_w^{1/2}$ for PNPMPA data of *Figure 1* according to equation (14)

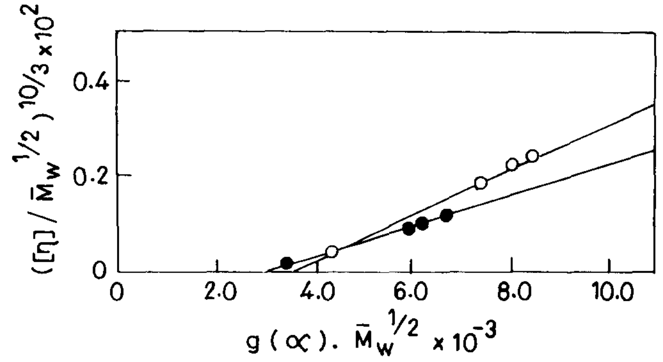

Figure 3 DB plot of $([\eta]/\bar{M}_w^{1/2})^{10/3}$ *versus* $g(\alpha)\bar{M}_w^{1/2}$ for PNPMPA data of *Figure 1* according to equation (17)

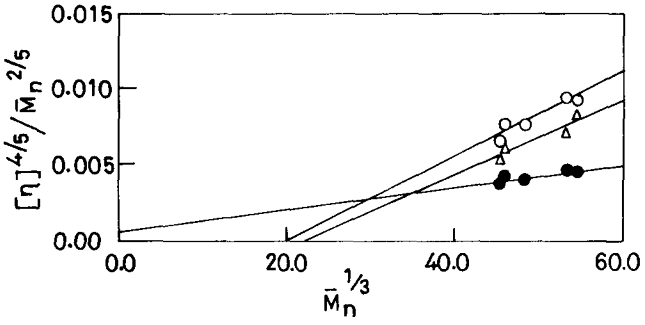

Figure 4 IP plot of $[\eta]^{4/5}/\bar{M}_n^{2/5}$ *versus* $\bar{M}_n^{1/3}$ for PNPA data in dioxane:toluene (v/v) mixtures 100:0 (○), 50:50 (△) and 30:70 (●) at 30°C according to equation (15)

Table 3 Characteristics of some excluded-volume theories

Theory	Power-type equation	ν_{max}	Equation number	Ref.
FFS	5	0.80	(7)	12, 13
KSR	3	1.00	(13)	14
BSF	3	1.00	(14)	15, 16
IP	3	1.00	(15)	2, 17
DB	10	0.80	(17)	18, 19
FOP	2	1.25	(20)	2
BJ	1	2.00	(21)	2

lower limit of ν comes out to be 0.5 in every excluded-volume theory; however, the upper limit (ν_{max}) varies according to the form of their $[\eta]$–M relationship. *Table 3* shows the values of ν_{max} in the respective α *versus* z relationship.

From *Tables 2* and *3* it is obvious that the value of ν for PNPA in 100% dioxane and 50:50 dioxane:toluene mixture exceeds the upper limit permitted by IP equation (15); hence its failure is reasonable. But in 30:70 dioxane:toluene mixture wherein ν is 1.0 (within ν_{max} for IP) and in the case of PNPMPA wherein ν values are well within DB's limitations, the failures of the corresponding theories need further explanation. At this juncture it must be emphasized that the constants, K and ν, in the MHKS relationship depend upon the polydispersities of the fractions[20,21], such that different pairs of K and ν can be obtained for different sets of fractions differing in respect of polydispersities of individual fractions for a given polymer–solvent system. During precipitation fractionation, higher heterogeneity is introduced in high-molecular-weight fractions. As a result ν derived from fractions with high polydispersities will be underestimated. It will be overestimated when $[\eta]$ is correlated with $\bar{M}_n$ in the MHKS plot. This probably explains the failure of DB and IP theories in the respective cases. The actual value of ν in the case of PNPMPA would turn out to be more than that permitted by DB theory, if fractions with low polydispersities are used in the analysis. Similarly, since the polydispersities of PNPA fractions are reasonably low, the use of $\bar{M}_n$ must have affected the determination of ν and K_θ. For 30:70 dioxane:toluene mixture, the value of K_θ obtained by the treatment of available $\bar{M}_w$ data, according to IP theory, matched well with that derived in later analysis by the Bueche–James theory. It is true that weight-average molecular weight is preferred[6,22] for a meaningful determination of MHKS constants, and hydrodynamic and configurational parameters, since it is close to the viscosity-average molecular weight. However, the same could not be done in the case of PNPA because inter- and intramolecular associations have been found to prevail in its solutions[11]. The resulting macromolecular clustering would lead to greater overestimation of weight-average molecular weight compared to its number-average counterpart. Therefore, number-average molecular weights are used in the case of PNPA.

The quality of a solvent and flexibility of polymer chains are interpreted in terms of ν. The PNPA chains having $\nu = 1.16$ in dioxane may be regarded, and rightly so, as semiflexible, in which case the results of first-order perturbation (FOP) and Bueche–James (BJ) theories[2], respectively given by:

$$\alpha^2 = 1 + 1.33z \tag{18}$$

$$\alpha^2 = 1 + 1.33\alpha z \tag{19}$$

can be used for estimating K_θ. Equations (18) and (19) can be translated into $[\eta]$–M form using equations (4) and (5). Thus FOP and BJ theories take the form:

$$\text{FOP} \quad [\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.44B\Phi_0 K_\theta^{-1/3} M^{1/2} \tag{20}$$

$$\text{BJ} \quad [\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.44B\Phi_0 K_\theta^{-2/3} (M[\eta])^{1/3} \tag{21}$$

Comparison of FOP with BSF in regard to the functional dependence of $[\eta]^{2/3}/M^{1/3}$ on M clearly indicates a wide spread of abscissa in FOP equation (20), and therefore a more accurate extrapolation to $M = 0$. For large excluded-volume effect, BJ equation (21) shows that $[\eta]^{2/3}/M^{1/3}$ is proportional to M, but at very small excluded volume it is proportional to $M^{1/2}$. This dependence is similar to that in equation (20), and also to FFS and KSR relations when excluded-volume effects are small. BJ theory is, therefore, found to be suitable for estimating K_θ for flexible-chain polymers also[21,23]. In BJ theory, which is meant for extremely rigid rod-like polymer molecules, the upper limit of ν is 2.0. Such molecules can be predicted to be incapable of exhibiting an excluded-volume effect under any condition. BJ theory thus appears to be an implausible result of the random flight model with Gaussian distribution. However, making use of its applicability, it is considered here for the sake of generality.

PNPA data, being well within the ν_{max} of FOP and BJ, adhere well to both the theories, as seen in *Figures 5* and *6*. It should be noted that a slight manipulation is generally required to make the extrapolated line intercept the ordinate at a common point. The plots are reasonably linear and yield reliable estimates of K_θ. However,

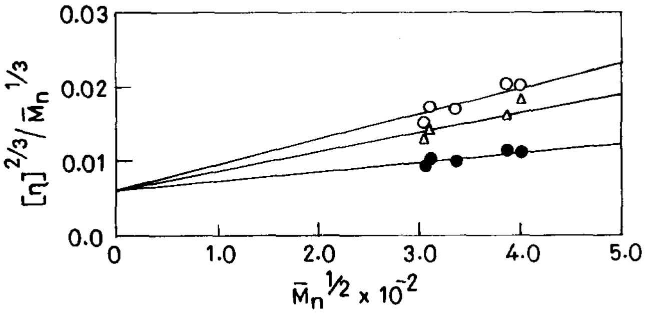

Figure 5 FOP plot of $[\eta]^{2/3}/\bar{M}_n^{1/3}$ *versus* $\bar{M}_n^{1/2}$ for PNPA data of *Figure 4* according to equation (20)

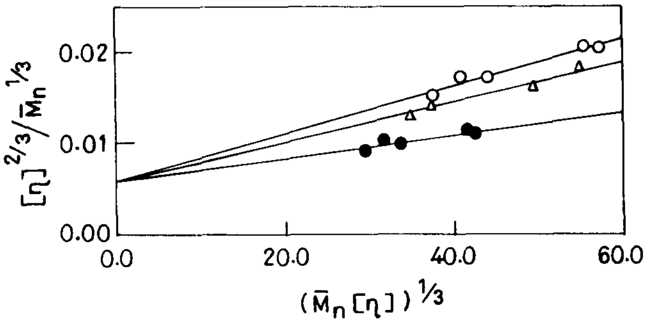

Figure 6 BJ plot of $[\eta]^{2/3}/\bar{M}_n^{1/3}$ *versus* $(\bar{M}_n[\eta])^{1/3}$ for PNPA data of *Figure 4* according to equation (21)

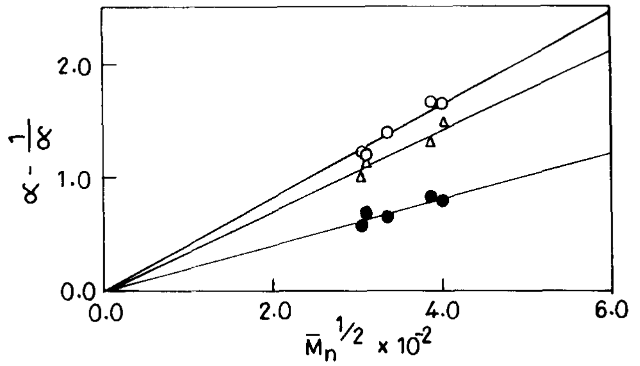

Figure 7 BJ plot of $\alpha - 1/\alpha$ *versus* $\bar{M}_n^{1/2}$ for PNPA data of *Figure 4* according to equation (19)

Table 4 Estimated values of K_θ at 30°C for PNPA and PNPMPA

		$K_\theta \times 10^4$ (dl mol$^{1/2}$ g$^{-3/2}$)					
Polymer	Solvent	FFS	KSR	BSF	IP	FOP	BJ
PNPA	Dioxane: toluene	–	–	–	–	4.65	4.65
PNPMPA	Dioxane: acetone	8.5	8.5	8.0	8.7	8.50	8.50

the solvent–polymer interaction parameter, B, which is discernible from the slopes of the extrapolated lines, is underestimated by FOP and still less estimated by BJ theory. This is an inherent character of these theories. Earlier reported data on cellulose triacetate and cellulose trinitrate were reanalysed according to equations (20) and (21). The values of K_θ thus obtained agreed very closely with those determined from the KSR relation, confirming the validity of these equations. The applicability of these theories in the case of polymers with ν values in the flexible range has already been demonstrated[1].

It is desirable to test the validity of these theories further by alternative methods. The procedures involve examining the linearity of the excluded-volume parameter z *versus* $M^{1/2}$ plots; or constructing theoretical plots of z *versus* α, or ε *versus* α, and then testing the adherence of the experimental data to the theoretical plots. Further, the excluded-volume theories essentially correlating α with z, which is proportional to $M^{1/2}$ through equation (5), are given by the closed approximate relations shown in equations (6), (10)–(12), (18) and (19). In all these relations some function of α is related with z. It is, therefore, possible to plot $F(\alpha)$ *versus* $M^{1/2}$, which should be linear in nature and pass through the origin. Alternatively, the ratio $F(\alpha)/M$ should be examined for its constancy.

An examination of the $F(\alpha)$ *versus* $M^{1/2}$ relationship in the present case showed that all the theories are fairly valid for the experimental data of PNPMPA. The situation, however, is different in the case of PNPA systems. The plots due to DB and BSF theories did not pass through the origin. Thus, the theories having third power (of α) or higher are found to be inadequate in explaining the excluded-volume effect operative in PNPA systems. On the other hand, plots due to BJ theory for these systems, as shown in *Figure 7*, are reasonably linear and pass through the origin as expected. Thus the validity of FOP and BJ theories for PNPA systems is further confirmed. In general, for small values of excluded volume ($z \leqslant 0.5$), all the theories agree closely, but for high excluded volume ($z \geqslant 0.5$) the theories differ appreciably and predict different values of the expansion parameter. It is this region of high excluded volume that is useful in selecting a theory for a particular system.

We now come to the last objective of this communication, i.e. estimation of K_θ. Both KSR and BSF (*Figures 1* and *2*) are applicable to PNPMPA data. Therefore, K_θ for this polymer is estimated from the intercepts of these plots and also from FOP and BJ theories. The values are listed in *Table 4*. For PNPA systems, although both FOP and BJ theories apply fairly well, statistical analysis has shown more reliability for the results obtained from BJ theory. Therefore, the intercepts due to BJ theory were determined by a linear regression analysis of data sets of 100:0, 50:50 and 30:70 dioxane:toluene mixtures. The intercepts were 0.00680, 0.00535 and 0.00585, respectively. The correction factor for determining 95% confidence intervals of these intercepts, as calculated statistically, are $\pm 4.83 \times 10^{-3}$, $\pm 4.89 \times 10^{-3}$ and $\pm 8.09 \times 10^{-4}$, respectively. As the theory predicts a common intercept for all the three sets of data, the small differences in intercept values are attributed to the uncertainties involved in the measurement of $[\eta]$ and $\bar{M}_n$. An arithmetic mean of these values ($= 0.0060$) is taken as the common intercept for all the three sets of data, and the plot (*Figure 6*) is manipulated accordingly. Then K_θ is estimated as 4.65×10^{-4} dl mol$^{1/2}$ g$^{-3/2}$.

It is not intended to stress the absolute values of K_θ of these polymers derived in this analysis, because the fractions do not encompass a wide range of molecular weights, which is generally desirable for such determinations. The values, nevertheless, are believed to be not too far from their exact values and can provide information regarding other molecular characteristics of the polymers.

CONCLUSIONS

The $[\eta]$–M relations based on two-parameter excluded-volume theories should not be indiscriminately applied to any solvent–polymer system for the determination of B or K_θ. Every theory is bound by an upper limit of MHKS constant, ν. Its validity for any solvent–polymer system will be decided by the experimental ν value, of the system under consideration, which should be well within the prescribed limit of the theory.

When the above criterion alone does not clarify the situation, polydispersities of the fractions, and type and range of molecular weights of polymer should be checked for the failure of theories.

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