

Viscosity Slope Constants for Solutions of Nylon 6 and Polytetrahydrofuran*

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Synopsis

Measurements of the viscosity slope constant k were made on solutions of nylon 6 and polytetrahydrofuran under different conditions of temperature, solvent, and molecular weight of polymer; θ -conditions were included so that the expansion factor α could be determined in each case. The value of k was influenced somewhat by the particular equation employed to derive it, and generally the Schulz-Blaschke equation (yielding k_{SB}) was the most reliable. Slope constants (k_{calc}) calculated according to an expression of Sakai were plotted as a function of α^3 and were compared with the corresponding curves in terms of experimental values of k . The agreement was moderately good for PTHF but poor in the case of nylon 6. An expression (due to Imai) involving experimental values of k and α was examined in order to establish a unique value of the slope constant k_θ under θ -conditions by an extrapolation procedure. Although individual values of k_θ for nylon 6 measured under θ -conditions were dependent on molecular weight, the Imai plot yielded a unique value of 0.50 and a slope similar in magnitude to that found for other polymer/solvent systems.

INTRODUCTION

The viscosity slope constant k has long been the object of diverse investigations including, for example, (i) its correlation with branching,¹ (ii) estimation of the solubility parameter of a polymer,² (iii) determination of the θ -composition of a mixed solvent,³ (iv) use in selecting appropriate solvent/precipitant ratios in fractional precipitation,⁴ (v) quantitative index of association,^{5,6,7} and (vi) correlation of k with the composition of a copolymer.⁸ None of these has been found entirely satisfactory, possibly on account of the somewhat empirical relations involved. Recently, Bohdanecký⁹ has reported on the behavior of k in relation to varying solvent power of the medium expressed in terms of the viscometric expansion factor α . As his report contains a comprehensive appraisal of the current situation, further introductory comment is superfluous here.

In the present communication, we have examined the effect of k introduced by varying the following: (i) nature of polymer, (ii) nature of solvent,

* Presented at the 9th I.U.P.A.C. Microsymposium on Macromolecules, "Thermodynamics of Interactions in Polymer Solutions," Prague, 1971.

(iii) molecular weight of polymer, and (iv) the temperature. The two polymers examined were polytetrahydrofuran and nylon 6. For the former, numerous liquids of different solvent power exist, and the θ -conditions are known.^{3,10,11,12} There is a more restricted range of single solvents for the latter, and the θ -conditions have not been established unambiguously, although a few have been proposed.¹³⁻¹⁵

The following abbreviations are adopted henceforth: PTHF, polytetrahydrofuran; DEM, diethyl malonate; *n*-BA, *n*-butanol; *n*-PA, *n*-propyl acetate; THF, tetrahydrofuran; MEK, methyl ethyl ketone.

EXPERIMENTAL

Materials

THF was purified and polymerized as described previously,¹¹ the molecular weight of the product, as determined¹⁶ from its intrinsic viscosity in toluene at 28°C, being 6.27×10^4 . Two fractions, of molecular weights 4.1×10^4 and 14×10^4 , were isolated by fractional precipitation from toluene solution with methanol at 25°C. During fractionation, an antioxidant (2,6-di-*tert*-butyl-*p*-cresol) was included in the solution.

The nylon 6 used as starting material was a sample of Maranyl F-500 (courtesy of Imperial Chemical Industries Ltd., Plastics Division). Fractionation from an initially 2% w/v solution of this polymer in *m*-cresol under a nitrogen blanket was effected at 23°C using cyclohexane as non-solvent. Cyanamid Antioxidant 2246 (2,2-dihydroxy-3,3-di-*tert*-butyl-5,5-dimethyldiphenylmethane) was included in the solution during fractionation. The fractions separated in the form of a coacervate and were finally isolated as a fine, white powder by adding an excess of diethyl ether to the coacervate. After several washings with diethyl ether to remove the *m*-cresol, the fractions were filtered and dried in vacuo at 40°C. The fraction of highest molecular weight thus obtained was subsequently re-fractionated in a similar manner into five subfractions. We consider this fractionation procedure for nylon 6 to be an improvement on the one employed previously.¹⁷ Molecular weights of the fractions were determined viscometrically in *m*-cresol at 30°C, using the Mark-Houwink relationship established by Tuzar, Kratochvíl, and Bohdanecký.¹⁸

Viscometry

Solution viscosity was measured in an Ubbelohde viscometer with a provision for filtration in situ (Polymer Consultants Ltd.). Kinetic energy and end-effect corrections were verified to be negligible and the temperature control was maintained within $\pm 0.1^\circ\text{C}$. The same antioxidants as used in the fractionations were incorporated into all solvents and solutions during viscometry, the concentrations being 0.17% w/v for PTHF and 0.1% w/v for nylon 6. In both cases the efficiency of the antioxidant in suppressing degradation was confirmed by redetermining the

intrinsic viscosity $[\eta]$ at a low temperature after measurements of it had been made on the same solution at higher temperatures. A dissolution time of 72 hr for nylon 6 was found to be essential in order to ensure complete solubility and reproducible flow times. The solvents, temperatures, and molecular weights of the fractions utilized are summarized in Table I.

Table I
Molecular Weights (M) of Polymers and Experimental Conditions for Viscometry

$M \times 10^{-4}$	Solvent	$T, ^\circ\text{C}$
PTHF		
4.1	toluene	28
4.1	CHCl_3 , THF, MEK	33.5
4.1	<i>n</i> -propyl acetate	15, 25, 35, 45
4.1	<i>n</i> -propyl acetate	55, 65, 75, 85
14	DEM	33.5 (θ)
14	DEM	38.3, 41.1, 46.2
14	DEM	53.0, 60.8, 64.7
14	DEM	69.3, 70.2, 75.3
14	DEM	81.5, 90.7
14	<i>n</i> -butanol	15, 31.3, 40.2
14	<i>n</i> -butanol	50.2, 60.0, 70.0
14	<i>n</i> -butanol	85.7
Nylon 6		
3.2, 6.0, 7.2, } 7.9, 9.5, 11.3, } 15.1, 17.0, 19.0 } " } " } " }	<i>m</i> -cresol	15, 30, 45, 60, 75, 90
	<i>m</i> -cresol	15, 30, 45, 60, 75, 90
	<i>m</i> -cresol	15, 30, 45, 60, 75, 90
	<i>m</i> -cresol/decalin (36/64 vol.)	30
	<i>m</i> -cresol/decalin (25/75 vol) (θ)	30
3.2, 7.9, 15.1, 19.0	<i>m</i> -cresol/decalin (30/70 vol)	30

θ -Conditions

DEM at 33.5°C was employed as θ -conditions¹¹ for PTHF. For nylon 6, the θ -composition at 30°C for the solvent/nonsolvent pair *m*-cresol/decalin was established as 25/75 v/v by means of the technique of Cornet and Ballegooijen.¹⁹

RESULTS

Experimental Slope Constants

The data were analyzed via the following common equations:

$$\eta_{sp}/c = [\eta] + k[\eta]^2c \quad (1)$$

$$(\ln \eta_r)/c = [\eta] - (0.5 - k)[\eta]^2c \quad (2)$$

$$0.5[(c/\eta_{sp}) + (c/\ln \eta_r)] = 1/[\eta] - (k - 0.25)c \quad (3)$$

$$\eta_{sp}/c = [\eta] + k[\eta]\eta_{sp} \quad (4)$$

The slope constant in eqs. (1) and (2) is normally designated as k_H , while the k in the Schulz-Blaschke²⁰ eq. (4) is commonly denoted by k_{SB} . In all cases, k_{SB} was found to be less than k_H . Thus, for PTHF the values of k_{SB} lay in the approximate range of 0.22 to 0.61, whereas the corresponding Huggins constants k_H were 0.29 to 0.96. For solutions of nylon 6, the values of k_H lay in what is considered to be the normal range of 0.22 to 0.55, with the k_{SB} values correspondingly ca. 0.1 lower in each case, i.e., from 0.13 to 0.46. For all systems, and irrespective of the plot used to derive k , the highest slope constants were exhibited under θ -conditions.

No specific attention will be paid to the slope constant derived from eq. (2), since its value was found to be practically identical with k_H derived from eq. (1). The values of k obtained from the Heller²¹ expression, eq. (3) (commonly denoted by k_{HEL}), lay in the range 0.26 to 0.64, but, as is evident from the form of this equation, they are rather tedious to calculate. Moreover, the plots of eq. (3), in common with those of eqs. (1) and (2), displayed some slight scatter at, and in the vicinity of, the θ -point. In contrast, the Schulz-Blaschke plots gave very good linearity under all conditions.

Comparison of Experimental and Calculated Slope Constants

One of the most successful equations proposed for calculating the slope constant (k_{calo}) is that due to Sakai²²:

$$k_{calo} = 0.5 + \bar{v}_2/2[\eta] - 3(\alpha^2 - 1)/4\alpha^4 \quad (5)$$

In eq. (5), \bar{v}_2 (ml/g) and $[\eta]$ (ml/g) are the partial specific volume of the polymer and the intrinsic viscosity, respectively, in the particular solvent used and at the specified temperature. The expansion factor α was calculated from eq. (6):

$$\alpha^3 = [\eta]/[\eta]_{\theta} \quad (6)$$

The partial specific volume and its temperature coefficient were taken as being the same as the specific volume and the coefficient of thermal expansion for amorphous polymer, values of 1.02 ml/g at 25°C and 8.0×10^{-4} ml/g/°C being utilized for PTHF.²³ Corresponding data for amorphous nylon 6 were not available and had to be interpolated as approximately 0.924 ml/g at 25°C and 4.8×10^{-4} ml/g/°C from thermal^{24,25} and x-ray²⁶ data in the literature. For a polymer of extremely low intrinsic viscosity, the second term on the right-hand side of eq. (5) assumes some significance relative to the total value of k_{calo} . For example, if \bar{v}_2 and $[\eta]$ are 1 ml/g and 0.1 dl/g, respectively, this term equals 0.05. However, for magnitudes of $[\eta]$ in question here, the term is very small and any uncertainties in the values of \bar{v}_2 and $d\bar{v}_2/dT$ do not affect k_{calo} to any critical degree.

Since the mode of plotting the viscometric data can yield small differences in the derived values of $[\eta]$ and k , it might be anticipated that these variations would be reflected in k_{calc} when obtained thereby from eq. (5). Similar considerations apply to the calculation of α . However, it may be seen from Figure 1 that the curve of k_{calc} as a function of α^3 is insensitive to such differences. No distinction between the two different polymers is made on the data points in this figure. Furthermore, when one particular type of plot is selected (the Schulz-Blaschke) and a distinction is made between the data for PTHF and nylon 6, a smooth curve is similarly displayed (Fig. 2).

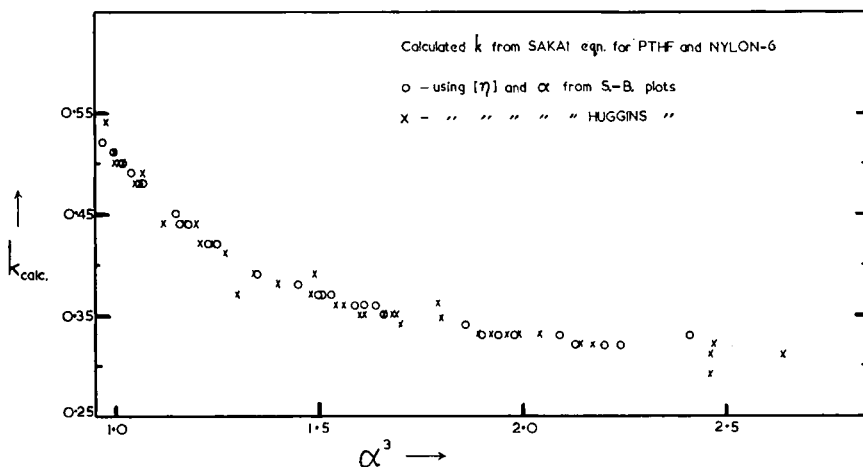


Fig. 1. Effect of viscosity equation used on plot of k_{calc} as a function of α^3 .

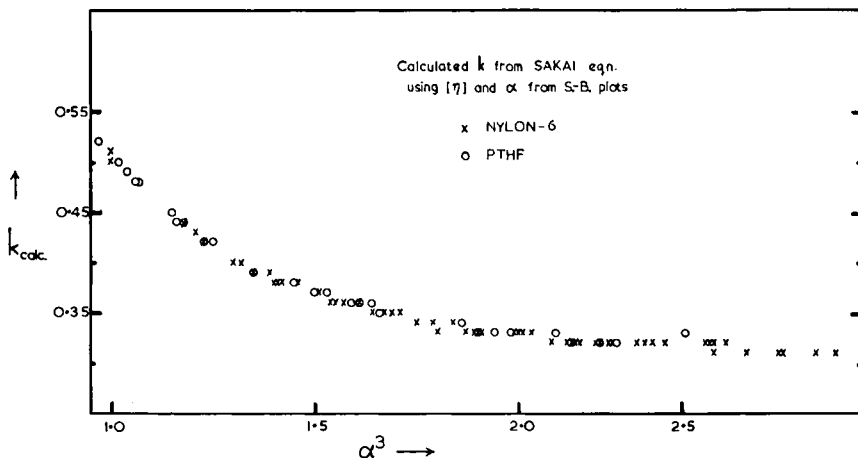


Fig. 2. Effect of the nature of the polymer on plot of k_{calc} as a function of α^3 .

We shall consider now the experimental slope constants in relation to their calculated values, the comparisons being made in Figures 3 and 4 for solutions of PTHF and nylon 6, respectively. The Schulz-Blaschke (S.-B.) plot has been utilized in Figure 3 both for constructing the full calculated curve and for the individual experimental data points. The S.-B. rather than the Huggins plots were invoked here because, as already intimated, the latter yield excessively high values of k in poor solvent

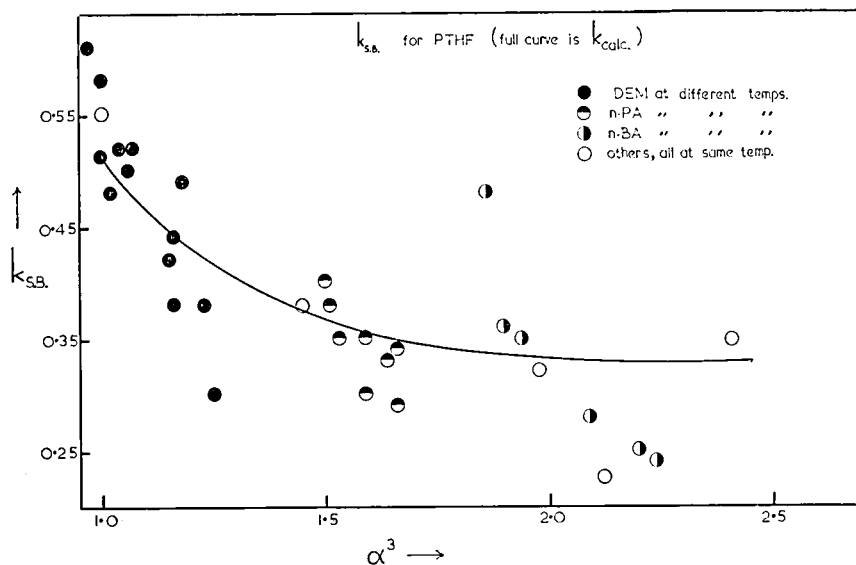


Fig. 3. Dependence of experimental values of k_{SB} on α^3 for solutions of PTHF.

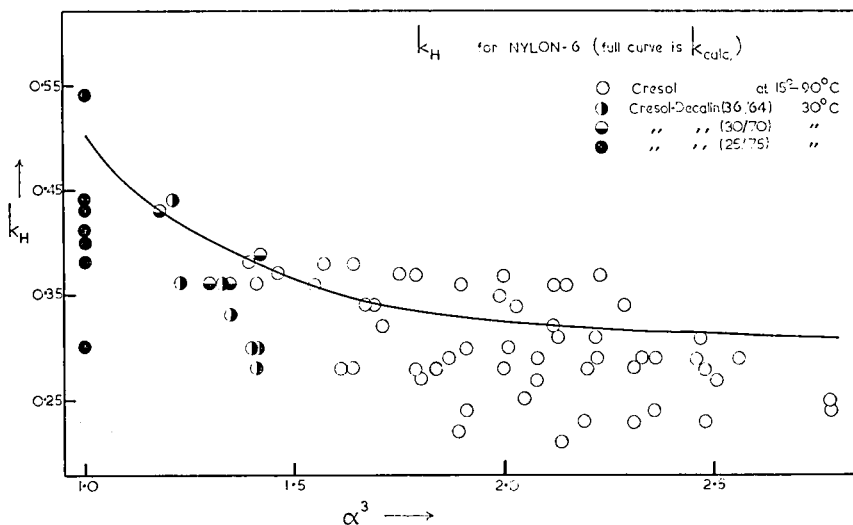


Fig. 4. Dependence of experimental values of k_H on α^3 for solutions of nylon 6.

media, and the values of k_θ are $\gg 0.50$. On the other hand, because the values of k_θ are $\ll 0.50$ when the S.-B. plot is employed for nylon 6 solutions, the data in Figure 4 are plotted in terms of the Huggins equation. Elaboration of the individual data in Figures 3 and 4 will be deferred to the discussion section, and it will only be noted here that the agreement between calculated and experimental curves is rather poor for both polymers.

DISCUSSION

In view of the fact that changes in k were deliberately effected by altering the conditions, any possible correlation of the slope constant with one of these conditions can only be attempted when the others are considered constant. In connection with some of the following specific observations on k , it may prove useful to recall our earlier findings²⁷ on the effect of temperature on $[\eta]$, with particular reference to those polymers (including PTHF and nylon 6) which possess a negative temperature coefficient of unperturbed dimensions. In simplest terms it was found that, as the temperature increases from the θ -temperature, the intrinsic viscosity can either (i) decrease or (ii) increase, pass through a maximum and then decrease.

Influence of Temperature (for a Fixed M and Given Solvent Medium)

For nylon 6 in *m*-cresol, measurements were made at six temperatures within the range 15–90°C and k_H increased from 0.25 to 0.36, corresponding to a fall in both α^3 and $[\eta]$. The highest k_H (= 0.43) was obtained in a θ -mixture, but this related to an intermediate temperature of 30°C, and θ -conditions could not be established by means of a temperature variation. On the assumption that hypothetical θ -conditions in *m*-cresol would obtain very much below 15°C (and actually lower than the freezing point), the highest value of the slope constant k_θ at this low temperature would *not* be assimilated into the trend for k to decrease with fall in temperature. Hence, the general inverse relation between $[\eta]$ and k becomes feasible for each of two distinct circumstances in isolation, namely, thermodynamically good and thermodynamically poor media.

For PTHF in *n*-PA, the situation is comparable with that just described for nylon 6 in *m*-cresol. Over a temperature range of 70°, the fall in $[\eta]$ was smaller than the corresponding one for nylon 6, and the total variation in α^3 was only from 1.66 to 1.51. Apart from a tendency for k to increase slightly with rise in temperature, no general conclusions can be drawn. The θ -temperature for PTHF in *n*-BA is not known, but is likely¹¹ to be in the region of 0–10°C. Measurements starting from a temperature slightly higher than this (15°C) and extending to 85.7°C demonstrated the strong thermodynamic effect on $[\eta]$, as opposed to the influence of chain flexibility. Thus, as the medium becomes thermodynamically better with rise in temperature, $[\eta]$ increases and k decreases. Were it not for the obstacle that the boiling point of *n*-BA is only 117.7°C, one could envisage that at

very high temperature there could well be a reversal of the situation, with chain flexibility assuming major importance resulting in a decrease in $[\eta]$ and an increase in k .

Such, in fact, is the case for solutions of PTHF in DEM on which measurements were made from the θ -temperature up to 90.7°C. The intrinsic viscosity rises, exhibits a maximum at ca. 65°C, and then falls at higher temperature. The corresponding behavior of k is also not uniform, but, in either a poor or a good medium individually, the value of k is in inverse relation to that of $[\eta]$. Thus, k decreases from 0.58 to 0.22 between 33.5° and 65°C and thereafter increases to 0.48 at 90.7°C.

Influence of Solvent (for Fixed M and Constant Temperature)

For solutions of nylon 6 at 30°C, the solvent medium was rendered gradually poorer by the inclusion of decalin into *m*-cresol. The resultant changes in k , $[\eta]$, and the Mark-Houwink exponent ν were noted. Taking the data for the fraction of $M = 15.1 \times 10^4$ by way of illustration, the value of k_B increased from 0.23 in *m*-cresol to 0.38 in the θ -mixture (ν was found to be 0.50 for the latter), and there was a corresponding decrease in $[\eta]$.

For PTHF, measurements were conducted in single solvents at 33.5°C in order to compare the results with those for DEM at this temperature. Results relating to solutions in toluene at 28°C (used to establish the molecular weight) were also included. The solvents were known from unpublished and published work to cover a wide spectrum from thermodynamically poor to thermodynamically good, viz., DEM, MEK, *n*-PA, *n*-BA, THF, chlorobenzene, and toluene. In the same order, the values of k_{SB} (and α^3) were 0.55(1.00), 0.38(1.45), 0.33(1.64), 0.48(1.86), 0.32(1.98), 0.22(2.13), and 0.35(2.41). Reference to these data, which are included in Figure 3, indicates that two of them (for chlorobenzene and *n*-BA) do not fall into the general pattern of the Sakai plot, but the trend is quite definite. No correlation between k_{SB} and the solubility parameter of the solvent could be established.

Effect of Molecular Weight

A constant value of k was not found for nylon 6 fractions under θ -conditions, where there was a trend for k_θ to increase with decrease in molecular weight (M). In the better solvent media, no obvious dependence of k on M could be detected. For PTHF in DEM at 33.5°, values of $k_{SB} = 0.55$ and 0.58 were obtained for the fractions of low and higher molecular weight, respectively. Such a difference is probably not significant, as it is marginally beyond the accuracy of $\pm 4\%$ with which k can be determined. Each of the other solvents for PTHF was used individually for the other fractions (Table I); but as there were only two values of M , it was not meaningful to investigate any possible dependence of k on molecular weight.

Slope Constant at the θ -Point

As just noted above, several values of k_θ (ranging from 0.30 to 0.54 on the basis of the Huggins plot) were obtained for nylon 6 solutions, and the highest of these values was similar to that found for k_θ in PTHF solutions. A unique value for k_θ has been predicted theoretically by Imai,²⁸ who derived the expression

$$k = k_\theta \alpha^{-4} + C_0 z \alpha^{-5} \quad (7)$$

where C_0 is a numerical constant and z is the excluded volume parameter. If z is expressed as follows in terms of α ,

$$\alpha^5 - \alpha^3 = C' z, \quad (8)$$

then eq. (7) becomes

$$k\alpha^4 = k_\theta + C_0'(\alpha^4 - \alpha^2). \quad (9)$$

In eqs. (8) and (9), C' and C_0' are numerical constants.

Plots of $k\alpha^4$ versus $(\alpha^4 - \alpha^2)$ for both polymers are shown in Figure 5, where k_H is employed as the slope constant. The intercept (k_θ) and slope (C_0') for nylon 6 are 0.50 and 0.29, respectively. Because the data for PTHF do not cover such a wide range of α , the plot is less well defined for it. If, as indicated the intercept is fixed as 0.50, the slope has a value of 1.1. However, the same slope as that obtaining for nylon 6 is produced if the intercept is taken as ca. 0.9 from the experimental k_H in DEM at 33.5 instead of by linear extrapolation. This is obviously a consequence of the fact that k_H was found to be greater than 0.50 for PTHF, even in moderately good solvents.

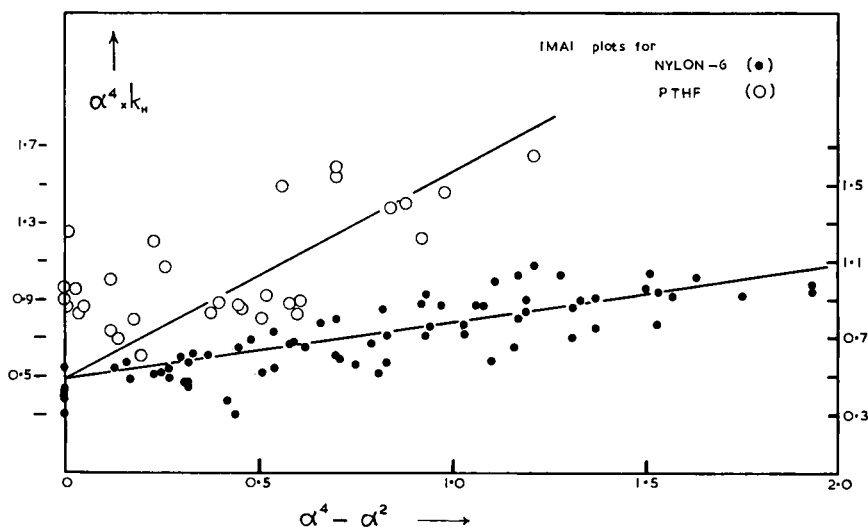


Fig. 5. Imai plots of $k\alpha^4$ as a function of $(\alpha^4 - \alpha^2)$ for solutions of PTHF and nylon 6.

When a similar plot (not illustrated) is constructed in terms of k_{SB} , the slope and intercept for PTHF are 0.24 and 0.52, respectively, whereas for nylon 6 they are 0.28 and 0.33, respectively. The last-mentioned of these (k_θ) derives from the fact that low values of k_{SB} were found for nylon 6 even in poor solvents.

In the original treatment by Imai, a value of 0.45 was predicted for k_θ , and this was asserted to be a unique value independent of temperature, nature of solvent and polymer, and molecular weight of polymer. Furthermore, in eq. (7), the excluded volume parameter was replaced by a quantity proportional to $M^{1/2}$, yielding the following expression in place of eq. (9):

$$k\alpha^4 = k_\theta + C_0' M^{1/2} \alpha^{-1}. \quad (10)$$

Employing literature values for monodisperse poly(α -methylstyrene)²⁹ and polydisperse polystyrene,³⁰ each in a single solvent but covering a wide range of molecular weights, Imai was able to demonstrate the validity of eq. (10), although the plots of $k\alpha^4$ versus $M^{1/2}\alpha^{-1}$ displayed some scatter. The extrapolated value of k_θ was approximately 0.45 in each case.

This type of plot for solutions of nylon 6 is illustrated in Figure 6, where the data points are seen to fall into two groupings, namely those for *m*-cresol and those for the poor solvent media. The form of the plots is similar to those obtained on adopting the Stockmayer-Fixman procedure³¹ under similar sets of conditions. Thus, the extrapolated intercept yields a quantity characteristic of the unperturbed state of the molecule, and the slope is dependent on the solvent power of the medium. In Figure 6, the data for the θ -mixture yield a line of slightly negative slope and an extrapolated intercept of ca. 0.45. The points for the moderately good solvents

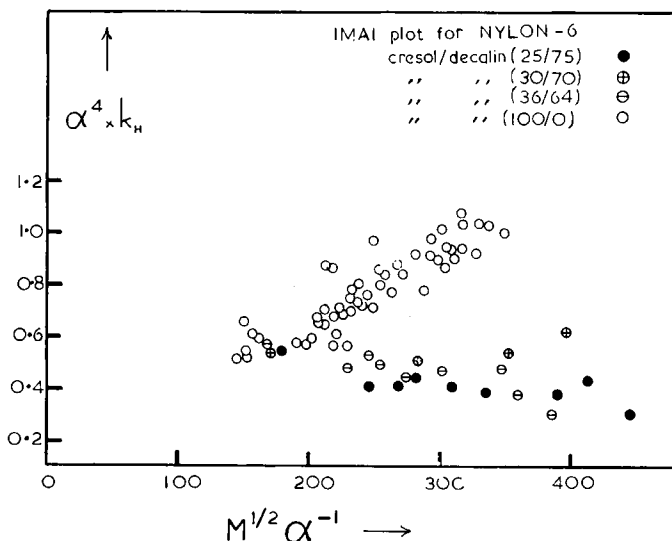


Fig. 6. Imai plots of $k\alpha^4$ as a function of $M^{1/2}\alpha^{-1}$ for solutions of nylon 6.

give rise to a greater slope, while the largest slope is exhibited by the points relating to the best solvent, *m*-cresol. A common intercept is not produced on extrapolation of the different sets of data, which actually intersect in the region of $k\alpha^4 = 0.50$ and $M^{1/2}\alpha^{-1} = 150$. Since the data for which $\alpha = 1$ comprise the interacting lines, the point of intersection corresponds to approximately $M^{1/2} = 150$, i.e., a degree of polymerization of about 200. It is only possible to speculate whether this is a critical chain length below which the slope constants assume a value characteristic of freely impenetrable spheres, but no measurements of k were made in good solvents for fractions of very low molecular weight.

CONCLUSIONS

An observation of fundamental importance lies in the difference noted (not for the first time) between k_{SB} and the slope constants determined from eqs. (1), (2), and (3). These equations and eq. (4) are actually all based on an expansion of the same power series limited to low values of c , the sole difference lying in the coordinates employed in the plots. While it has been seen that this difference does not influence the calculated Sakai plots, it does have a bearing on the corresponding experimental curves. Thus, k_{SB} was utilized for PTHF solutions because the k_H values were considered higher than the acceptable range. Likewise, the k_H values were employed for the other polymer since the k_{SB} values lay below this range. The precise definition of this acceptable range is still not unambiguously resolved. Thus, for fractions of poly(α -methylstyrene) in a good solvent, Noda et al.²⁹ reported $0.4 > k_H > 0.3$, and under θ -conditions, $1.45 > k_H > 0.55$. For polystyrene in cyclohexane, Orofino³² obtained $k_H = 0.68$ at the θ -temperature, but this value increased steadily to 0.95 on lowering the temperature to 19° below the θ -temperature. In the present work, we have accepted the result of a recent analysis by Sakai,³³ according to which the semiempirical bounds for k_θ are 0.52–0.56. It is not clear why values above this range should be obtained for PTHF solutions if the Huggins rather than the Schulz-Bluschke plots are employed.

When *both* terminal carboxyl and amino groups are present in nylon 6, the resultant association has been demonstrated^{4,6,34} to yield an increase in k to values far in excess of 0.56. In the solutions utilized here, there is no evidence of this. In dilute solutions of poly(ethylene oxide), the existence of hydrogen bonding between terminal hydroxyl groups and main-chain oxygen atoms has been demonstrated,³⁵ but no viscosity slope constants were measured. In solutions of PTHF in several solvents (not comprised solely of θ -solvents), Elias and Adank³⁶ obtained values of k_H greater than 1.1. To account for this, a solvent-induced helical structure involving weak induction forces between the protons of the methylene groups and the main-chain oxygen atoms was proposed. There does not yet appear to be sufficient evidence to support this attractive hypothesis,

and, furthermore, there are no clear chemical and structural differences between the solvents reported to promote this effect and those which do not.

Association and induced structures have just been noted as possible influences on k in certain instances, although almost certainly not in the present context. In view of this, any far-reaching conclusions on the general significance of k must be treated with caution and the usefulness of the slope constant considerably diminished. In general terms, the following comments may be made: (i) k can be determined to within a maximum accuracy of $\pm 4\%$, and any changes induced in k by external factors can only begin to be considered meaningful if in excess of this amount; (ii) k is unsuitable as a reliable means of estimating $[\eta]$ by the single-point procedure, whereby $[\eta] = [-1 \pm (1 + 4k\eta_{sp})^{1/2}]/2kc$; and (iii) the marked changes in k in the region where α varies most markedly make the slope constant an insensitive means of detecting the θ -point.

Financial support and a maintenance grant (to R.W.R.) from the Science Research Council are gratefully acknowledged. We should like to express our thanks to Mr. M. Ertleman for careful experimental assistance and for carrying out the numerical calculations.

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Received January 13, 1972