

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Unperturbed Dimension of Polymer Molecules from Viscosity Measurements in Mixed Solvents. II

Subasini Lenka^a; Padma L. Nayak^a; Sanjay K. Nayak^a

^a Laboratory of Polymers and Fibres Department of Chemistry, Ravenshaw College, Cuttack, Orissa, India

To cite this Article Lenka, Subasini , Nayak, Padma L. and Nayak, Sanjay K.(1984) 'Unperturbed Dimension of Polymer Molecules from Viscosity Measurements in Mixed Solvents. II', *Journal of Macromolecular Science, Part A*, 21: 1, 57 – 68

To link to this Article: DOI: 10.1080/00222338408065905

URL: <http://dx.doi.org/10.1080/00222338408065905>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Unperturbed Dimension of Polymer Molecules from Viscosity Measurements in Mixed Solvents. II

SUBASINI LENKA, PADMA L. NAYAK, and SANJAY K. NAYAK

Laboratory of Polymers and Fibres
Department of Chemistry
Ravenshaw College
Cuttack 753003, Orissa, India

ABSTRACT

An expression for the Flory constant ϕ is derived according to which ϕ should depend on the polymer-solvent pair and the temperature. The variations of ϕ , $[\eta]$, and k , the latter two being fundamental terms in the equation, $C/\eta_{sp} = 1/[\eta] - kC$, are utilized for the determination of the unperturbed dimension of polymer molecules in solution. The importance of k , and the alternative expression which has been derived for k , are discussed.

The determination of the unperturbed dimension of polymer molecules from viscosity measurements of dilute polymer solutions is of much importance in view of the new complications arising from the diverse results obtained in theoretical and practical studies. The theories relating the intrinsic viscosity, molecular weight and the expansion parameter α are inadequate to explain all the factors involved in the study of dimensional properties in solution. Recently, we have reported the relationship between $[\eta]$ and k for a polymer in

a series of solvents based on the procedure followed by Bhatnagar et al. [2] and pointed out that the slope of the linear relationship of $[\eta]^{-1}$ and k should afford a method of determining the unperturbed dimensions of polymer molecules. The conclusion was based on the concept of the existence of a common cross-over point concentration in the plot of C/η_{sp} versus C in a series of solvents. In this communication the values of $(\bar{r}_0^2/M)^{1/2}$ have been determined in some mixed solvents from the plots of $1/[\eta]$ versus k , irrespective of the linearity of such a plot or the existence of a common cross-over point concentration.

THEORETICAL DEDUCTIONS

In a previous communication we deduced

$$\frac{C}{\eta_{sp}} = \frac{1}{[\eta]} - \frac{1}{(1 + \gamma/RT)} C \quad (1)$$

where

$$[\eta] = 9.347 \times 10^{20} \{ (\bar{r}_0^2)^{3/2} / M \} \alpha^3 (1 + \gamma/RT)$$

and

$$\gamma = E_2 - E_1 - E_{12}$$

The E 's are the molar energies of activation of viscous flow of solvent (E_1), solute (E_2), and E_{12} arising due to nonideality of polymer solution.

In this derivation, the concentration dependence of the expansion parameter was neglected. Comparing this expression with the corresponding expression,

$$[\eta] = \phi (\bar{r}_0^2 / M)^{3/2} M^{1/2} \alpha^3 \quad (2)$$

it is seen that

$$\phi = 9.347 \times 10^{20} (1 + \gamma/RT) \quad (3)$$

Since $(1 + \gamma/RT)$ is dependent on the solvent and the temperature for an individual polymer, it can be said that ϕ should also behave in a simple manner. This goes against the concept of an inversal constant,

as suggested by Fox and Flory [3], having a value of 2.1×10^{21} . The fact that the variation in η with solvent and temperature should depend only on the extent of variation of the expansion parameter, α in solution, seems untenable. Views concerning this fact have been expressed by Gardner [4], Zimm [5], Kurata and Stockmayer [6], and Ptitsyn and Eisner [7]. It has been shown [6, 7] that ϕ should decrease from a value of 2.87×10^{21} at the Θ temperature to a value as low as 1.86×10^{21} for a very high value of expansion parameter α . As for the expression of η , it seems that this extra variation in η may be explained in the term $(1 + \gamma/RT)$. For a polymer, η_{Θ} has a value dependent only on the molecular weight and the unperturbed dimension as revealed in the expression

$$[\eta]_{\Theta} = \phi_{\Theta} (\bar{r}^2/M)^{3/2} M^{1/2} \quad (4)$$

It is therefore evident that $(1 + \gamma/RT)$ will assume a definite value at the Θ temperature or in a Θ solvent. Since $\alpha = 1$ when $[\eta] = [\eta]_{\Theta}$ we have,

$$[\eta]_{\Theta} = 9.347 \times 10^{20} (\bar{r}_0^2/M)^{3/2} M^{1/2} (1 + \gamma/RT)_{\Theta} \quad (5)$$

By comparing Expression (5) with Expression (4) and taking $\phi_{\Theta} = 2.87 \times 10^{21}$, one obtains,

$$(1 + \gamma/RT)_{\Theta} = 3.077$$

Let us now examine to what extent our previous equation for the linearity holds true. We have

$$[\eta] = 9.347 \times 10^{20} (\bar{r}_0^2/M)^{3/2} M^{1/2} \alpha^3 (1 + \gamma/RT) = P_0 \alpha^3 / k$$

where

$$P_0 = 9.347 \times 10^{20} (\bar{r}_0^2/M)^{3/2} M^{1/2}$$

$$\frac{d[\eta]^{-1}}{dk} = P_0^{-1} \left[\alpha^{-3} - 3k\alpha^{-4} \frac{d\alpha}{dk} \right] \quad (6)$$

From the above expression it is clear that a plot of $[\eta]^{-1}$ versus k should not be linear. It can be linear with a slope equal to P_0^{-1} only when

$$\frac{d\alpha}{dk} = \frac{\alpha - \alpha^4}{3k} \quad (7)$$

Now, the slope at $k = 3.25$ and $\alpha = 1$ is evidently

$$\frac{d[\eta]^{-1}}{dk} = P_0^{-1} \left[1 - 0.975 \frac{d\alpha}{dk} \right]_{k=0.325}$$

where $k = 0.325$ and $\alpha = 1$.

If it is arbitrarily assumed that when $\alpha = 1$, $d\alpha/dk = 0$, as required in Eq. (7), then

$$\frac{d[\eta]^{-1}}{dk}_{k=0.325} = P_0^{-1}$$

or

$$(\bar{r}_0^2/M)^{1/2} = 2.204 \times 10^{-8} (M/P_x)^{1/3} \quad (8)$$

where

$$P_x = P_0 \times 10^3$$

Equation (8) is exactly analogous to our previous equation

$$(\bar{r}_0^2/M)^{1/2} = 2.204 \times 10^{-8} (M/C_0)^{1/3}$$

where C_0 is the cross-over point concentration in g/mL or the slope of $[\eta]^{-1}$ versus k plot. The only difference is that the present consideration has a usefulness slope only at $k = 0.325$, in contrast to our previous report of the linearity of the $[\eta]^{-1}$ versus k plot.

Most of the data available in the literature for $[\eta]$ and k are derived from the linear relationship of η_{sp}/C versus C and extrapolation to zero concentration in view of the requirements of Huggins' equation [8]. Bhatnagar et al. [2] derived Huggins' equation by considering viscous flow as a rate process, and they deduced

$$\eta_{sp}/C = [\eta] + \left\{ 0.5 - \frac{0.5}{(1 + \gamma/RT)^2} \right\} [\eta]^2 C \quad (9)$$

and

$$k_{\text{(Huggins)}} = 0.5 - \frac{0.5}{(1 + \gamma/RT)^2}$$

This expression for k allows 0.5 as the maximum value of k . There is, however, ample evidence that k differs significantly from this limit, especially for feebly polar and polar polymers. Our expression $(1 + \gamma/RT)$ suffers from no such limitation and can have any positive value up to unity. Of course, it is not clear at this stage whether the term γ/RT contains all the specific interactions k is supposed to involve. The fact is that values of $[\eta]$ and k obtained from C/η_{sp} versus C differ significantly from the values obtained from η_{sp}/C versus C plots. In view of these facts we determined the values of $[\eta]$ and k from the corresponding Huggins' values as follows:

- (i) From the values of $[\eta]$ and k , the slopes of Huggins' plots were obtained.
- (ii) Knowing the slopes and intercepts, the values of η_{sp}/C at arbitrary concentrations were determined and hence the values of $[\eta]^{-1}$ and k were obtained from C/η_{sp} versus C plots.

Values of $[\eta]^{-1}$ were plotted against k values and the ordinates at $k = 0.325$ were obtained to determine the unperturbed dimensions from the relationship

$$(\bar{r}_0^2/M)^{1/2} = \left\{ \frac{[\eta]_{k=0.325}}{2.87[M]^{1/2}} \right\}^{1/3} \times 10^{-7} \quad (10)$$

DISCUSSION

It is reasonable to assume that the solvent and temperature variation of $[\eta]$ cannot only be hydrodynamic and be explained in terms of ϕ only. The inclusion of the term $1 + \gamma/RT$ in $[\eta]$ and k suggests that the solvent and temperature dependence of η and k has to be explained from the viewpoint of both hydrodynamics and thermodynamics. The Flory theory of rate process points out that the solvent and temperature dependence of ϕ , the so-called Flory constant, cannot be ignored. The factor $(1 + \gamma/RT)$, a sort of extra interaction term, may involve many specific interactions between polymer and solvent and temperature. Most of the data taken from the literature include polymers which contain more or less polar groups, and since fairly good values of the

unperturbed dimensions are obtained, it seems that $(1 + \gamma/RT)$ also includes effects due to electrical interactions [9]. However, it is not possible to assess this view at present. Though the values of unperturbed dimensions obtained by the present procedure agree well with the values obtained by conventional methods, it will be seen that in all cases the values are higher than the literature values. One reason for this may be the fact that the values of $[\eta]$ obtained by C/η_{sp} versus C of η_{sp}/C versus C are always greater than the corresponding values obtained from a Huggins' plot in mixed solvents.

The importance of k for the determination of the unperturbed dimension needs special mention since the accuracy of the values of $(\bar{r}_0^2/M)^{1/2}$ depends to a greater extent on the accuracy of the expression and determination of k . We are now in a position to examine the relative merits of the expressions for k derived on the basis of the theory of rate processes.

In our derivation of $k = 1/(1 + \gamma/RT)$, we deduced,

$$\eta_{rel} = e^{X_2\gamma/RT} [1 - X_2 \{1 - w(p)F(y)\}]^{-1}$$

and kept up to the first power in X_2 . If one keeps all terms up to the first power in X_2 , the following expression is obtained for k .

$$K = (1 + \gamma/RT)^{-1} \left\{ 1 + \frac{\gamma^2/2R^2T^2}{1 + \gamma/RT} \right\}$$

when

$$w(p) F(y) \ll 1, = 0.5 + \frac{0.5}{(1 + \gamma/RT)^2} \quad (11)$$

It is evident that this expression only allows values of k which are greater than 0.5, and these are not the normal values of k . Although mathematically sound, the inclusion of the second-order term in X_2 does not improve the value of k . A third expression for k may be derived starting from the expression of η_{rel} given by Bhatnagar et al., i.e.,

$$\eta_{rel} = e^{X_2\gamma/RT} [1 + X_2 \{1 - w(p)F(y)\}]$$

The expression for C/η_{sp} obtained from the above expression is

$$C/\eta_{sp} = 1/[\eta] - \frac{(\gamma/RT) \{1 + \gamma/2RT\}}{(1 + \gamma/RT)^2} C$$

when

$$w(p) F(y) \ll 1$$

so that

$$k = 0.5 - \frac{0.5}{(1 + \gamma/RT)^2} \tag{12}$$

In Figs. 1 and 2 the values of $[\eta]^{-1}$ are shown in the same plot for

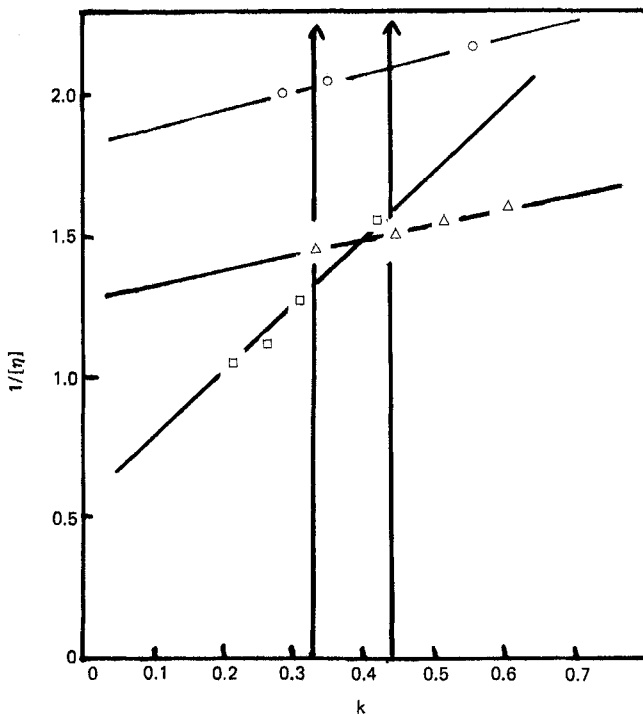


FIG. 1. Plot of $[\eta]^{-1}$ versus k for the mixed solvent methanol-toluene (50:50). (○) Temperature = 26°C. (△) Temperature = 30°C. (□) Temperature = 35°C.

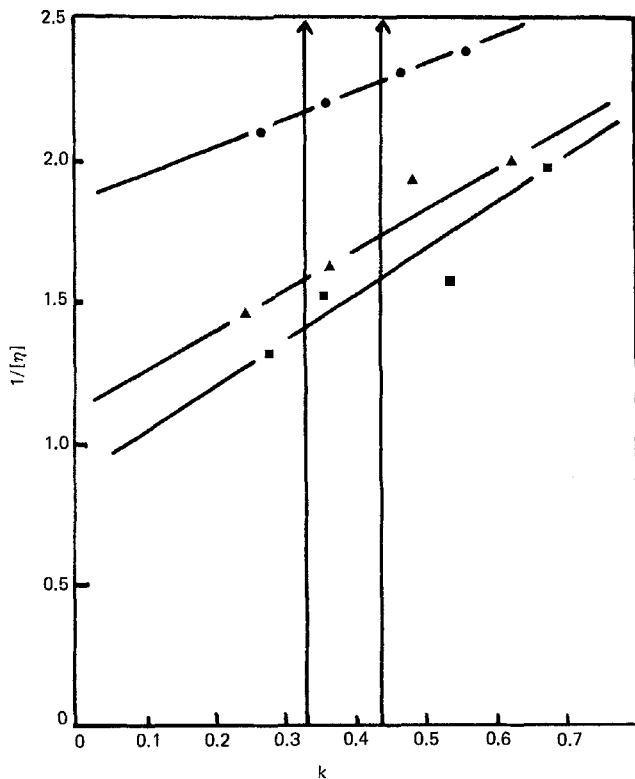


FIG. 2. Plot of $[\eta]^{-1}$ versus k for the mixed solvent methanol-toluene (65:35). (●) Temperature = 26°C. (▲) Temperature = 30°C. (■) Temperature = 35°C.

$k = 0.325$ and $k = 0.447$, the only difference being that the $1/(1 + \gamma/RT)$ values now represent the values of k given by Expression (12). The values of $(\bar{r}_O^2/M)^{1/2}$ (Tables 1-6) are found to be higher than the literature values [10, 11]. This increase of $(\bar{r}_O^2/M)^{1/2}$ values might be due to the decrease in the denominator of Eq. (10). A rigorous test for the expression of k may lie in the calculation of the expansion parameter α which will be reported in a future communication.

TABLE 1. Variation of $[\eta]^{-1}$ with k for Poly(methyl Methacrylate) in Methanol and Toluene (50:50) at 26°C^a

Fraction	$1/[\eta]$	k	$[\eta]_\Theta$		$(\bar{r}_0^2/M)^{1/2} \times 10^{27}$	
			a	b	a	b
I	2.000	0.294				
II	2.092	0.321	0.487	0.471	1127	1114
III	2.222	0.401				
IV	2.272	0.552				

^aa = values corresponding to $k = 0.325$. b = values corresponding to $k = 0.447$.

 TABLE 2. Variation of $[\eta]^{-1}$ with k for Poly(methyl Methacrylate) in Methanol and Toluene (50:50) at 30°C^a

Fraction	$1/[\eta]$	k	$[\eta]_\Theta$		$(\bar{r}_0^2/M)^{1/2} \times 10^{27}$	
			a	b	a	b
I	1.4306	0.346				
II	1.4666	0.450	0.689	0.666	1131	1118
III	1.652	0.521				
IV	1.800	0.613				

^aa and b as in Table 1.

TABLE 3. Variation of $[\eta]^{-1}$ with k for Poly(methyl Methacrylate) in Methanol and Toluene at 35°C^a

Fraction	$1/[\eta]$	k	$[\eta]_\Theta$		$(\bar{r}_o^2/M)^{1/2} \times 10^{27}$	
			a	b	a	b
I	1.176	0.220				
II	1.282	0.275				
III	1.333	0.312	0.740	0.625	1085	1026
IV	1.538	0.428				

^a a and b as in Table 1.

TABLE 4. Variation of $[\eta]^{-1}$ with k for Poly(methyl Methacrylate) in Methanol and Toluene (65:35) at 26°C^a

Fraction	$1/[\eta]$	k	$[\eta]_\Theta$		$(\bar{r}_o^2/M)^{1/2} \times 10^{27}$	
			a	b	a	b
I	2.127	0.285				
II	2.222	0.352				
III	2.272	0.471	0.456	0.442	1125	1122
IV	2.380	0.623				

^a a and b as in Table 1.

TABLE 5. Variation of $[\eta]^{-1}$ with k for Poly(methyl Methacrylate) in Methanol and Toluene (65:35) at 30°C^a

Fraction	$1/[\eta]$	k	$[\eta]_\Theta$		$(\bar{r}_0^2/M)^{1/2} \times 10^{27}$	
			a	b	a	b
I	1.470	0.259				
II	1.639	0.376	0.632	0.588	1109	1083
III	1.923	0.491				
IV	2.083	0.631				

^a a and b as in Table 1.

 TABLE 6. Variation of $[\eta]^{-1}$ with k for Poly(methyl Methacrylate) in Methanol and Toluene (65:35) at 35°C^a

Fraction	$1/[\eta]$	k	$[\eta]_\Theta$		$(\bar{r}_0^2/M)^{1/2} \times 10^{27}$	
			a	b	a	b
I	1.315	0.275				
II	1.562	0.351				
III	1.666	0.547	0.714	0.636	1113	1071
IV	1.960	0.682				

^a a and b as in Table 1.

REFERENCES

- [1] P. L. Nayak, S. Lenka, and M. Dash, J. Macromol. Sci.-Chem., **A19**, 321 (1983).
- [2] H. L. Bhatnagar, A. B. Biswas, and M. K. Gharpurey, J. Chem. Phys., **28**, 88 (1958).
- [3] P. J. Flory and T. G. Fox, J. Am. Chem. Soc., **23**, 1904 (1951).
- [4] P. L. Auer and C. S. Gardner, J. Chem. Phys., **23**, 1545 (1955).
- [5] A. H. Zimm, J. Chem. Phys., **24**, 269 (1956).
- [6] K. Kurata and W. Stockmayer, Fortschr. Hochpolym.-Forsch., **3**, 193 (1963).
- [7] A. B. Ptitsyn and Y. E. Eizner, J. Phys. Chem. USSR, **32**, 2464 (1958).
- [8] H. L. Huggins, J. Am. Chem. Soc., **64**, 2716 (1942).
- [9] G. A. I. Goring and A. Rezanowich, J. Colloid Sci., **15**, 472 (1960).
- [10] N. R. Krigbaum, L. Mandelkern, and P. J. Flory, J. Polym. Sci., **9**, 381 (1952).
- [11] A. N. Chinai, J. D. Matlack, A. Resmick, and R. J. Samuels, Ibid., **17**, 391 (1951).

Accepted by editor May 12, 1983

Received for publication June 20, 1983