

A SECOND APPROXIMATION TO THE ANGULAR DISTRIBUTION FUNCTION FOR THE SCATTERING OF LIGHT BY MACROMOLECULES IN GOOD SOLVENTS

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A new approximation to the light scattering angular distribution function for polymers in good solvents is proposed and applied to experimental results obtained from a very high-molecular-weight polystyrene fraction. Close agreement with a more laborious, but more accurate, method for finding average coil dimensions is obtained.

Since the first implied suggestion that light scattering might be used for the determination of molecular weights,¹¹ and the reformulation of the problem with special reference to the polymer molecule by Debye,¹² the theory of light scattering has been extended to cover finite concentrations of polymer,⁵ polydisperse polymers,⁸ and branched polymers.⁸ These treatments, however, have all been based on the assumption of an intersegmental distance relationship of the form

$$\langle r_{ij}^2 \rangle = k |i-j|, \quad (1)$$

(i and j being any two segments in the chain and $\langle r_{ij}^2 \rangle$ the mean square distance between them). It is known¹³ that this relationship only holds in an ideal (Θ) solvent, where the second virial coefficient is zero, and breaks down in other solvents. In a good solvent, the mean square end-to-end distance will be much greater than that given by eqn. (1). Recently there have been three attempts to extend the theory of light scattering to polymers in good solvents, i.e. where the intersegmental distance is given by

$$\langle r_{ij}^2 \rangle = k |i-j|^{1+\nu} N^{\varepsilon-\nu} \quad (2)$$

(i and j being any two segments, N , the total number of segments and k , ν and ε constants).

Two of them^{3,4} involve mathematical approximations and the assumption that $\nu = \varepsilon$, and the third² is exact for monodisperse polymers.

In this paper, a closer approximation than that given by Benoit⁵ for the scattering of light by a polymer in a good solvent is proposed and applied to some results previously analyzed by other methods.

THEORETICAL

Consideration of the scattering of light by a random coil in which the average distance between segments i and j is given by eqn. (2) leads^{1,2,3,4} to the following expression for the angular distribution factor⁵ $P(\theta)$ for sufficiently large values of N :

$$P(\theta) = 2 \int_0^1 (1-x) \exp(-ux^{1+\nu}) dx, \quad (3)$$

$$x = |i-j|/N, u = \left\{ \frac{4\pi \sin(\theta/2)n}{\lambda} \right\}^2 \frac{\langle R^2 \rangle}{6};$$

λ = wavelength of light used; θ = angle of observation; n = refractive index of medium, $\langle R^2 \rangle$ = mean square end-to-end distance of coil.

It is interesting to note that ε does not occur in this expression and so the end-to-end distance against molecular-weight relationship cannot be found from light scattering if the intersegment distance relationship is of the form assumed.

Benoit³ has shown that this expression may be expanded to give

$$P(\theta) = \frac{2\kappa}{u^{2\kappa}} \int_0^u u^\kappa e^{-y} y^{\kappa-1} dy - \frac{2\kappa}{u^{2\kappa}} \int_0^u y^{2\kappa-1} e^{-y} dy$$

$$= 2u^{-\kappa} \kappa! - 2\kappa u^{-2\kappa} (2\kappa-1)! - 2\kappa u^{-\kappa} (\kappa-1, u)! + 2\kappa u^{-2\kappa} (2\kappa-1, u)!, \quad (4)$$

where $\kappa = 1/(1+\nu)$ and $y = ux^{1+\nu}$,

and $(t, q)! = \int_q^\infty p^t e^{-p} dp$.

The last two terms involve incomplete factorial functions⁶ which may be integrated by parts to give asymptotic expansions, the early terms of which are small compared with the two complete factorials, provided u is large enough.

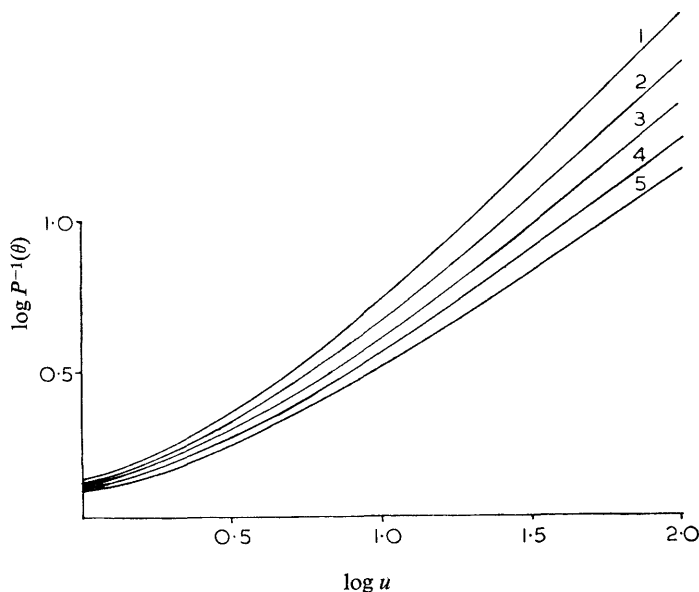


FIG. 1.—Log $P^{-1}(\theta)$ against log u for computed values of $P(\theta)$ and u .

The approximation presented in this paper is concerned with sufficiently large values of u and we shall neglect these terms in the rest of the discussion. Hence

$$P(\theta) \simeq 2u^{-\kappa} \kappa! \left\{ 1 - \frac{2\kappa-1}{\kappa-1} u^{-\kappa} \right\}. \quad (5)$$

Benoit³ has pointed out that for large values of u , a plot of $\log 1/P(\theta)$ against $\log u$ (or in experimental practice $\log \sin^2(\theta/2)$) will give a straight line of slope κ . Fig. 1 is a graph of $\log P^{-1}(\theta)$ against $\log u$ for various values of ν , plotted from the table of exact values of $P(\theta)$, for various values of ν , computed previously.²

These plots are roughly linear at large values of u , but curve appreciably at smaller values. All deviate from linearity at values of u less than about 20 and even above this value the slopes of the lines are in poor agreement with the known values of ν (see table 1). Over the limited ranges of u met with experimentally, the curve may be approximated by a straight line but the slope of such a line may be considerably smaller than the limiting slope and will therefore lead to a value of ν greater than the true one. Hence, for a reasonably accurate determination of ν ,

values of u greater than 20 are required. Unfortunately, however, this corresponds to an r.m.s. end-to-end distance of the polymer chain of about 2700 Å, i.e. to a D.P. of 6.7×10^4 or m.w., 2.7×10^6 , even under the best observational conditions (violet or shorter wavelength light and high-scattering angles). The polymer used by Loucheux, Weill and Benoit,¹⁴ and ourselves⁷ has in fact a molecular weight greater than this, but is well above the size of polymers normally under investigation. Serious errors may arise if Benoit's approximation is used to determine ν in the wrong range of u .

TABLE 1

curve	1	2	3	4	5
ν	0.0	0.1	0.2	0.3	0.4
ν from graph	0.01	0.129	0.229	0.337	0.46

In order to obtain a more accurate value of ν , it is proposed that account should be taken of the second term in eqn. (4) and (5), i.e. the second complete factorial function. To determine ν to this approximation, a plot of $\log \{P^{-1}(\theta)[1 - (u^{-\kappa}(2\kappa-1)!/(\kappa-1)!)]\}$ against $\log u$ is required. Fig. 2 shows this plot for hypothetical monodisperse polymers with various values of ν . The factor in square brackets has been calculated using the value of ν obtained from the limiting slope of the curves of fig. 1.

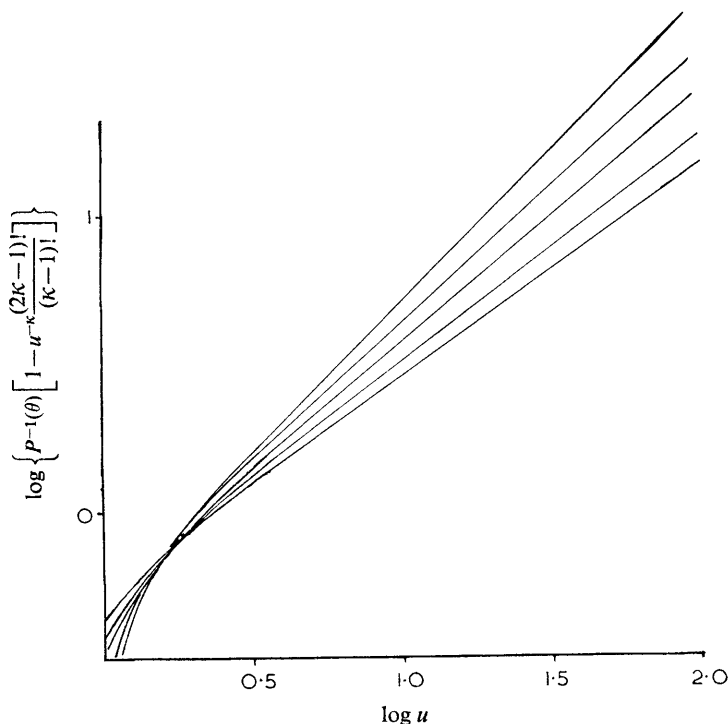


FIG. 2.— $\log \{P^{-1}(\theta)[1 - u^{-\kappa}(2\kappa-1)!/(\kappa-1)!]\}$ against $\log u$ for computed values of $P(\theta)$ and u .

The curves of fig. 2 are linear down to u values of about 3 and the slopes give the correct values for ν .

Whilst this lower value of u is still in the range of large polymers ($\langle R^2 \rangle^{\frac{1}{2}} \sim 1000$ Å, D.P. $\sim 10^4$, m.w. $\sim 3 \times 10^5$ – 10^6) even for the best conditions of measurement, it

covers a range extending well below the extreme sizes where the first approximation is valid.

Consideration of practical polydisperse systems introduces some difficulty. As Loucheux, Weill and Benoit have shown,¹⁴ the determination of ν using the first approximation is independent of the polydispersity of the polymer. This is not the case for the second approximation here presented. To apply the second approximation to experimental results we have to find a first approximation to $[1 - (u^{-\kappa}(2\kappa-1)!/(\kappa-1)!)]$. In this expression, u should contain the number average mean square end-to-end distance of the polymer $\langle R^2 \rangle_N$. However, the value of $\langle R^2 \rangle$ that we have from the slope of the tangent to the $P^{-1}(\theta)$ curve at $u = 0$ is that of a polymer with average molecular weight somewhat higher than the Z average (or for a Θ solvent it is actually $\langle R^2 \rangle_Z$), called hereafter $\langle R^2 \rangle_{LT}$ or $\langle R^2 \rangle_{Z+}$. In addition, the value of ν which we must use is obtained from the first approximation and will in general be too small. This means that $(2\kappa-1)!/(\kappa-1)!$ will be smaller than the true value for the system and $u^{-\kappa}$ will contain a value of $\langle R^2 \rangle$ which is too large, but this will be partly compensated by using an exponent κ which is too small. The extent of cancellation of these errors could only be assessed if the true values of ν and u were known.

EXPERIMENTAL AND RESULTS

In this section the approximation has been applied to the measurements on a very high m.w. polystyrene in M.E.K. and benzene which were previously analyzed² using a graphical method based on tables of exact values of $P(\theta, \kappa)$ for a monodisperse polymer.² In addition, measurements of the same polystyrene in a benzene + methanol mixture which have not been published before, have been evaluated by the method used previously and the present method.

The polymer fraction used by Loucheux, Weill and Benoit¹⁴ was the same as that used in our⁷ experiments but had been precipitated and purified several times more and so was probably a somewhat sharper fraction.⁹

The relevant unknowns κ , $\langle R^2 \rangle_W$, M_N , $\langle R^2 \rangle_{LT}$ and M_W were found in the following way. First, using the usual Zimm plot,⁵ values of $\langle R^2 \rangle_{LT}$ and M_W were found from the slope of the limiting tangent and the intercept of the $P^{-1}(\theta)$ curve at $u = 0$. A graph of $\log(c/I)_{c \rightarrow 0}$ against $\log \sin^2(\theta/2)$ was then drawn, following Benoit,³ and the slope of this at large values of $\log(c/I)_{c \rightarrow 0}$ gave the first approximation to the value of ν .

Values of the factor $[1 - u^{-\kappa}(2\kappa-1)!/(\kappa-1)!]$ based on the above values of $\langle R^2 \rangle$ and ν were then calculated for the various angles at which observations were made. A graph of $\log \{P^{-1}(\theta)[1 - u^{-\kappa}(2\kappa-1)!/(\kappa-1)!]\}$ against $\log \sin^2(\theta/2)$ was then plotted, the slope of which gave a new value of ν . Finally, from the slope of the tangent at $\sin^2(\theta/2) = 0$ and the slope and intercept on the $P^{-1}(\theta)$ axis of the asymptote to a graph of $P^{-1}(\theta)$ against $[\sin^2(\theta/2)]^\kappa$ the ratio of M_W/M_N and an upper limit for the ratio M_{Z+}/M_W were found, the latter via $\langle R^2 \rangle_{Z+}/\langle R^2 \rangle_W$.¹⁴ An upper limit for M_{Z+}/M_W can be found since we do not know ϵ but only ν . Fig. 3, 4 and 5 show the above graphs for the polystyrene fraction in the benzene + methanol (80:20) mixture and table 2 shows the values obtained for $\langle R^2 \rangle_{LT}^\dagger$, M_W , κ (1st approx.), κ (2nd approx.), M_W/M_N and $\langle R^2 \rangle_W^\dagger$ in the three solvents.

TABLE 2

solvent	second virial coefficient	M_W	$\langle R^2 \rangle_{LT}^\dagger$ Å	ν first approx.	ν second approx.	M_W M_N	$\langle R^2 \rangle_W^\dagger$ Å	M_{LT} M_W
benzene	1.55×10^{-4}	10.7×10^6	5440	0.25	$0.12 \pm .03$	1.35	5260	1.04
methyl ethyl ketone	0.49×10^{-4}	9.7×10^6	4010	0.28	$0.20 \pm .05$	1.43	4014	1.0
benzene + meth- anol mixture	0.51×10^{-4}		4121	0.22	$0.15 \pm .04$	1.53	4025	1.04

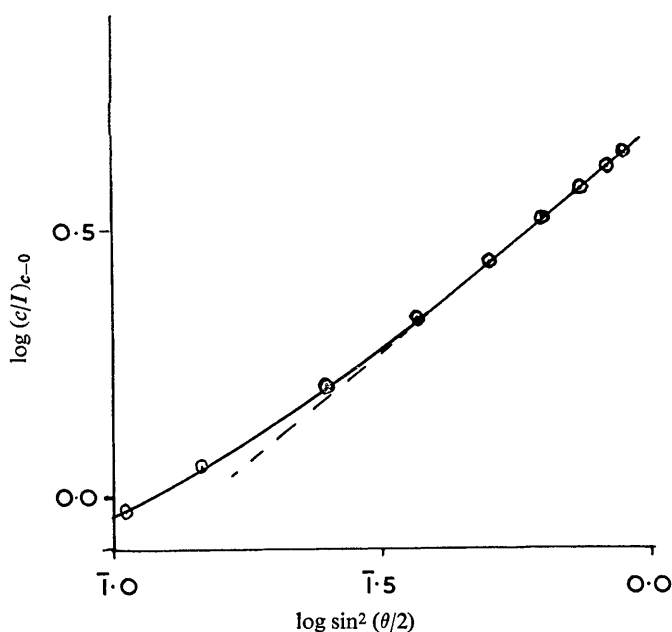


FIG. 3.— $\log(c/I)_{c=0}$ against $\log \sin^2(\theta/2)$ for polystyrene in the benzene+methanol mixture.

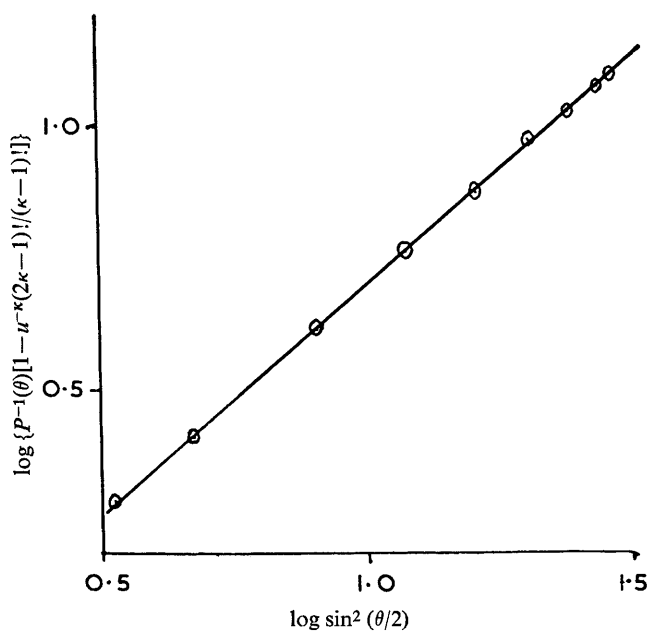


FIG. 4.— $\log \{P^{-1}(\theta)[1-u^{-\kappa}(2\kappa-1)!/(\kappa-1)!]\}$ against $\log \sin^2(\theta/2)$ for polystyrene in the benzene+methanol mixture.

As pointed out before,² the location of the tangent to the $P^{-1}(\theta)$ curve at zero angle presents some difficulty due to the presence of a point of inflection in the curve which may be partially masked by curvature caused by polydispersity. The value of $\langle R^2 \rangle_{LT}$ quoted has been calculated directly from the slope of the tangent at $\sin^2(\theta/2) = 0$ to a $P^{-1}(\theta)$ curve which has been deliberately extrapolated without change of sign of the radius of curvature; no attempt has been made to estimate the position of the inflection. The

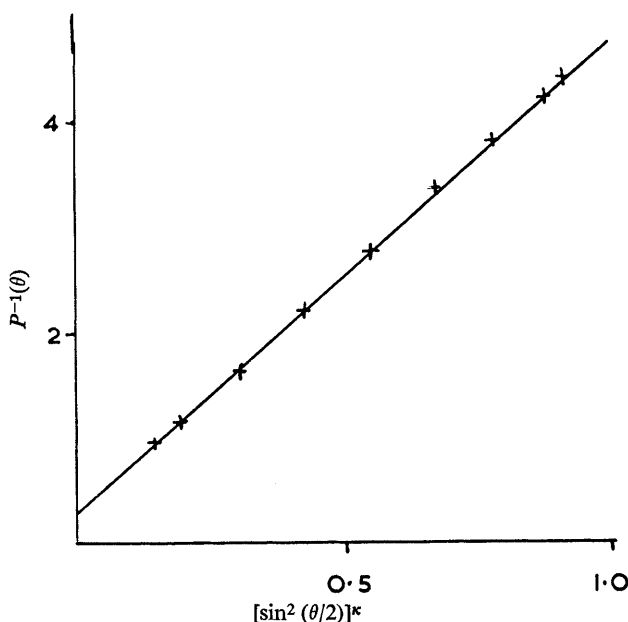


FIG. 5.— $P^{-1}(\theta)$ against $[\sin^2(\theta/2)]^\kappa$ for polystyrene in the benzene+methanol mixture.

formula first derived by Peterlin¹ connecting this slope and $\langle R^2 \rangle_{Z+}$ has not been used (the ordinary Debye formula has been applied) since the slope at the origin of the curve we have drawn is certainly greater than the true slope of the $P^{-1}(\theta)$ curve and application of Peterlin's formula would make the derived value of $\langle R^2 \rangle$ even greater.

Fig. 6 shows the Zimm plot for the polystyrene fraction in the benzene+methanol mixture and fig. 7 the graph of $u^{1/2}/\sin(\theta/2)$ against ν constructed from the values of $P^{-1}(\theta)$ from the Zimm plot as previously described.² The curves in fig. 7 should intersect at a point for a monodisperse polymer. Although this method of finding ν does not appear, in this case, to give a value for ν so precisely as for the other two solvents,² a value of 0.16 ± 0.02 is indicated.

DISCUSSION

The values of ν found by the two methods and the ratios M_w/M_N and M_{Z+}/M_w found in the three solvents by the second approximation are in reasonable agreement, and indicate that within the accuracy of the experiment and theoretical assumptions there is little to choose between the two methods of finding ν .

The order of values of ν obtained in the three solvents is, however, at variance with what one would expect from consideration of the second virial coefficients, and with values of ϵ obtained from consideration of the exponent in viscosity against molecular weight relationships.⁴ The latter would give $\epsilon = 0.16$ in benzene and $\epsilon = 0.05$ in M.E.K.

There are three possible explanations for the discrepancies. First, it is possible that the simultaneous presence of polydispersity and excluded volume effects

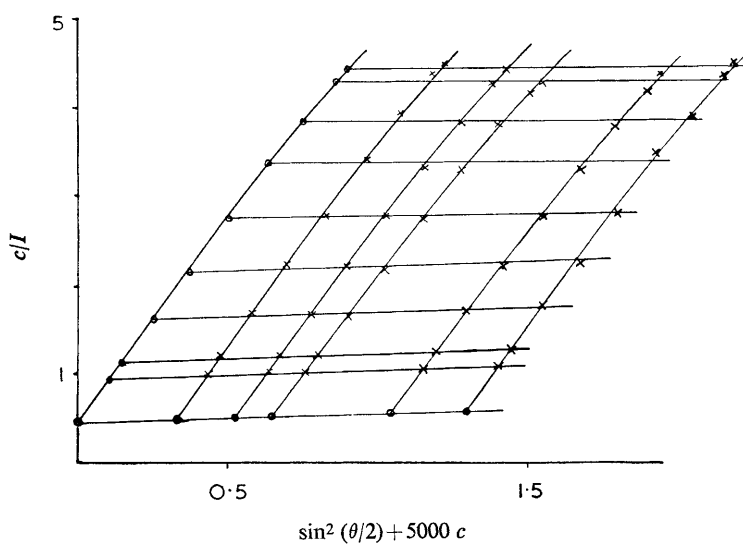


FIG. 6.—Zimm plot for polystyrene in the benzene+methanol mixture.

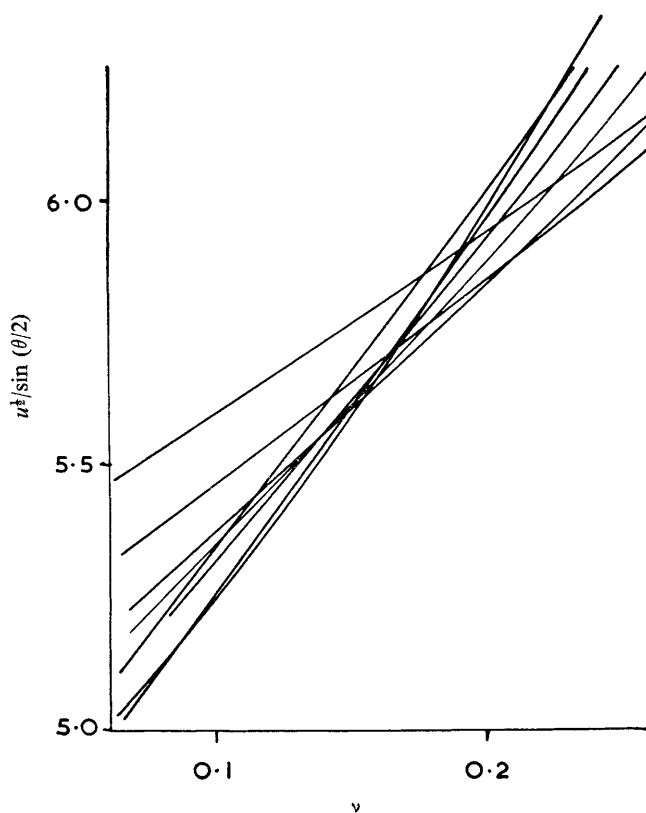


FIG. 7.— $u^{1/2}/\sin(\theta/2)$ against v for polystyrene in the benzene+methanol mixture.

(especially at small values of v) influence the $P^{-1}(\theta)$ curve in such a way that the two effects cannot really be separated. Secondly, the intersegmental distance relationship we have used may be at fault, and thirdly, it may be that the range of u values covered in the poor solvents does not extend to high enough values of u to give a good value of v .

The first explanation almost certainly applies to the method described by Hyde, Ryan, and Wall since monodispersity is assumed in their treatment, but, as Benoit has shown, should not apply to the first approximation, nor to any great extent to the present approximation. The second objection is certainly valid. A better form of intersegmental distance relationship is available from experiments on random walks in a lattice,¹⁰ but is rather too cumbersome for use in the light-scattering theory and would probably not affect the scattering greatly. The last explanation may apply to the low angle points in the poor solvents but should not greatly affect the determination of v .

The difference between the value of v for polystyrene in benzene obtained by the second approximation (0.12) and that obtained by the first (0.25) gives some measure of the difference between the two approximations, although some difference in values is obtained between our method of applying the first approximation and the slightly different method used by Benoit.

The agreement in values of v derived from the method² which assumes monodispersity and the second approximation, which does not, is, however, extremely puzzling and indicates that great care should be taken in applying the methods at small values of v and u , i.e. in bad solvents.

The suggested new approximation for evaluating the sizes of polymer molecules in good solvents by light-scattering methods probably goes as far as it is worthwhile going in this direction at the present time. Further development will depend on more accurate knowledge of the segmental distribution in polymer molecules.

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