The Application of the Ptitsyn Theory to Viscosity Data for Amylose and Amylose Acetate in Various Solvents*

W. BANKS and C. T. GREENWOOD

The Ptitsyn relation for the excluded volume effect has been combined with various expressions relating α *to* α_η. *When the resultant equations were tested using viscosity–molecular weight data for amylose acetate and amylose in various solvents, the most satisfactory results were obtained using the Kurata–Stockmayer–Roig expression, i.e.* $\alpha^{5/2}=\alpha_\eta^3$. *This combination of relations described the experimental data over a larger molecular weight range than did the Stockmayer–Fixman treatment. Furthermore, the unperturbed dimensions of amylose obtained from an approximate form of the Ptitsyn–Kurata–Stockmayer–Roig treatment were within three per cent of the experimentally determined value.*

IN the past few years much attention has been paid to the problem of the excluded volume in polymer solutions. The original Flory theory[1], which postulated that in the limiting case of an exceedingly good solvent $[\eta] \propto M^{0\cdot8}$, has been challenged by a number of other theories[2-4]. The latter are known collectively as the 'third-power law theories', because they lead in the limit of a good solvent to a direct proportionality between $[\eta]$ and M. Two of these third-power law theories have been extensively tested—namely those developed by Kurata and Stockmayer[2], and by Stockmayer and Fixman[3] —because their mathematical form enables the unperturbed dimensions of the macromolecule to be estimated from measurements carrried out in good solvents. Although early work appeared to confirm their validities, more recent results[5,6] have shown that the range of molecular weights over which they may be successfully applied is quite small.

The remaining theory of the 'third-power law' group was developed by Ptitsyn[4], but the mathematical form of the final equation relating the expansion factor α to the molecular weight is such that it cannot be used in determining unperturbed dimensions from measurements carried out in good solvents. (An approximate form of the Ptitsyn equation which permits this procedure will be examined later.) This doubtless accounts for the rather limited use of this theory, since in order to test its validity, measurements have to be carried out in a number of solvents (including a theta-solvent), and then the expansion factor is related to the molecular weight.

We have recently completed a series of measurements on native amylose and amylose acetate in various solvents, and wish to present here an analysis of the data according to the Ptitsyn relation.

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EXPERIMENTAL AND RESULTS

The fractionation of linear potato amylose, its conversion to the triacetate, and the physical measurements carried out on the fractions have been reported in detail elsewhere[6–8].

The following relations were found (where $[\eta]$ is expressed in ml/g) for amylose acetate in the molecular weight range $(0{\cdot}15–3{\cdot}15)+10^6$:

$$[\eta]_1 = 9{\cdot}16 \times 10^{-2}\overline{M}_w^{0{\cdot}50} (\text{solvent} = \text{nitromethane}/n\text{-propanol } 43{\cdot}3:56{\cdot}7,\ \text{v/v})$$

$$[\eta]_2 = 1{\cdot}70 \times 10^{-2}\overline{M}_w^{0{\cdot}66} (\text{solvent} = \text{nitromethane}/n\text{-propanol } 50:50,\ \text{v/v})$$

$$[\eta]_3 = 8{\cdot}50 \times 10^{-3}\overline{M}_w^{0{\cdot}73} (\text{solvent} = \text{nitromethane})$$

For amylose in the molecular weight range $(0{\cdot}08–1{\cdot}80) \times 10^6$, the relations were:

$$[\eta]'_1 = 1{\cdot}15 \times 10^{-1}\overline{M}_w^{0{\cdot}50} (\text{solvent} = 0{\cdot}33\ \text{M potassium chloride})$$

$$[\eta]'_2 = 3{\cdot}05 \times 10^{-2}\overline{M}_w^{0{\cdot}62} (\text{solvent} = \text{formamide})$$

$$[\eta]'_3 = 1{\cdot}51 \times 10^{-2}\overline{M}_w^{0{\cdot}70} (\text{solvent} = \text{dimethylsulphoxide})$$

$$[\eta]'_4 = 8{\cdot}36 \times 10^{-3}\overline{M}_w^{0{\cdot}77} (\text{solvent} = 0{\cdot}15\ \text{M potassium hydroxide})$$

In this paper 'smoothed' values of $[\eta]$, i.e. those generated using the above relations, are used throughout. Values of $\overline{M}_w$ for insertion in these equations were within the range examined experimentally, and were chosen to give an even spread of the results shown in *Figures 1–4.*

DISCUSSION

The linear expansion factor (α), defined by

$$\alpha^2 = \overline{r^2}/\overline{r_0^2} \qquad (1)$$

where $\overline{r_0^2}$ is the mean-square end-to-end distance of the polymer coil in a theta-solvent, and $\overline{r^2}$ is the corresponding value in a good solvent, is, in all the present theories, a function of a single variable, z, where

$$z = (\tfrac{3}{2}\pi)^{3/2}\, B\, (M/\overline{r_0^2})^{3/2}\, M^{\frac{1}{2}} \qquad (2)$$

where B is a solvent–solute interaction parameter. Perturbation theory has related α exactly to z by

$$\alpha^2 = 1 + (\tfrac{4}{3})\, z - 2{\cdot}08\, z^2 + \ \ldots \qquad (3)$$

Unfortunately, the slow convergence of this series limits the applicability of the relation to an exceedingly narrow range of small z. Different treatments have yielded different closed expressions for α: that due to Ptitsyn[4] has the form

$$\alpha^2 = [3{\cdot}68 + (1 + 9{\cdot}36z)^{2/3}]/4{\cdot}68 \qquad (4)$$

According to equation (4), a graph of $[(4{\cdot}68\,\alpha^2 - 3{\cdot}68)^{3/2} - 1]$ as a function of $M^{\frac{1}{2}}$ should yield a straight line passing through the origin.

Expansion coefficients are usually obtained from measurements of limiting viscosity numbers in various solvents, including of course a theta-solvent. The expansion factor (α_η) is then defined by

$$\alpha_\eta^3 = [\eta]/[\eta]_\theta \tag{5}$$

where $[\eta]$ is the limiting viscosity number in a good solvent, and $[\eta]_\theta$ is the corresponding value in a theta-solvent.

Some dubiety exists regarding the relation between α and α_η. The most widely-used relations are those due to (a) Flory, in which

$$\alpha = \alpha_\eta \tag{6}$$

(b) Kurata, Stockmayer and Roig[9] according to which

$$\alpha^{5/2} = \alpha_\eta^3 \tag{7}$$

and (c) the Stockmayer–Fixman relation[3] in which

$$(\alpha_\eta^3 - 1)/1{\cdot}55 = (\alpha^3 - 1)/2 \tag{8}$$

In this paper, each of the relations (6)–(8) is used in conjunction with the Ptitsyn equation (4).

(a) $\underline{\alpha = \alpha_\eta}$

With this identity (4) becomes

$$(4{\cdot}68\,\alpha_\eta^2 - 3{\cdot}68)^{3/2} - 1 = 9{\cdot}36z \tag{9}$$

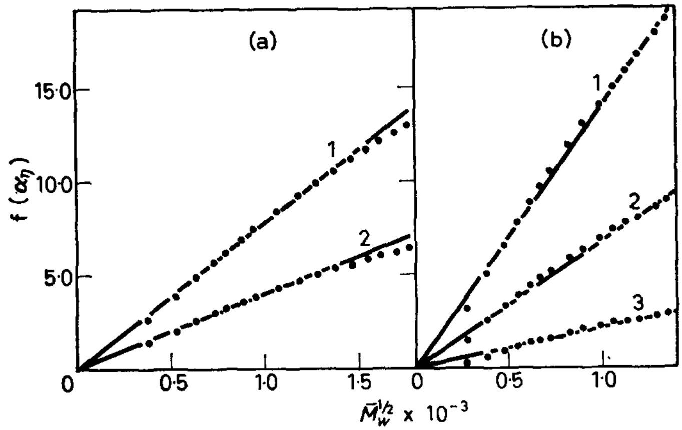

Figure 1—Graph of $f(\alpha_\eta)$ against $\bar{M}_w^{1/2}$, where $f(\alpha_\eta) = (4{\cdot}68\,\alpha_\eta^2 - 3{\cdot}68)^{3/2} - 1$ [see equation (9) of text]: (a) Amylose acetate in (1) nitromethane, and (2) nitromethane/propanol (50:50, v/v); (b) Amylose in (1) 0·15 M KOH, (2) dimethylsulphoxide, and (3) formamide

Figure 1(a) shows the data for amylose acetate graphed according to (9) and *Figure 1*(b) the corresponding plot for amylose. In both cases the graphs are obviously curved over the entire molecular weight range. However, for the interval $(0{\cdot}4\text{–}1{\cdot}8) \times 10^6$, the data approximate to a straight line. Because the measurements on the acetate extend to a higher molecular weight, the curvature is emphasized at this end of the scale; conversely, for the amylose the curvature appears more pronounced in the region of low molecular weight as more measurements were carried out in this region. From *Figure 1*(b) in particular it is obvious that (9) is invalid in the region of low molecular weight.

(b) $\alpha^{5/2} = \alpha_\eta^3$

Substitution of (7) in (4) yields

$$(4{\cdot}68\,\alpha_\eta^{2{\cdot}4} - 3{\cdot}68)^{3/2} - 1 = 9{\cdot}36z \tag{10}$$

The data for amylose and amylose acetate, graphed according to (10) are shown in *Figures 2*(a) and *2*(b). Again, the graphs are curved but, in contrast to *Figure 1*, the curvature is less pronounced in the region of high molecular weight.

(c) $(\alpha_\eta^3 - 1)/1{\cdot}55 = (\alpha^3 - 1)/2$

Substitution of (8) in (4) gives

$$[4{\cdot}68\,(1{\cdot}290\alpha_\eta^3 - 0{\cdot}290)^{2/3} - 3{\cdot}68]^{3/2} - 1 = 9{\cdot}36z \tag{11}$$

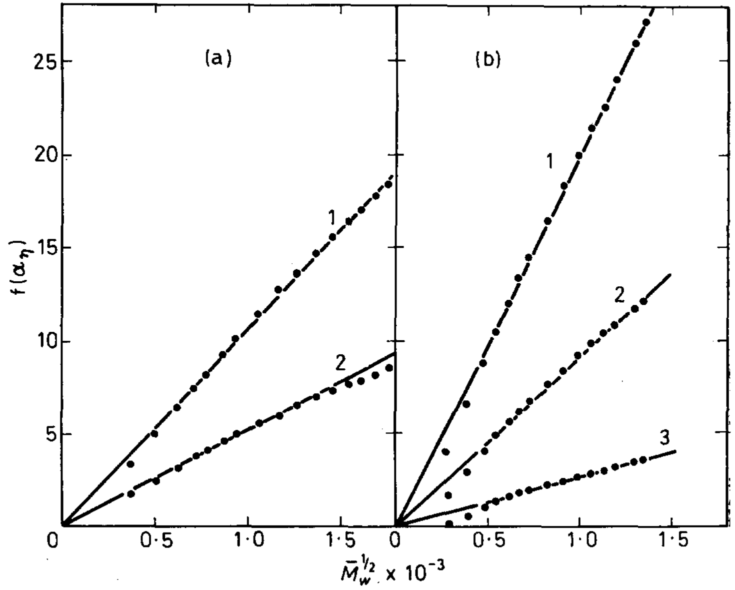

Figure 2—Graph of $f(\alpha_\eta)$ against $\bar{M}_w^{1/2}$, where $f(\alpha_\eta) = (4{\cdot}68\,\alpha_\eta^{2{\cdot}4} - 3{\cdot}68)^{3/2} - 1$ [see equation (10) of text]: (a) Amylose acetate in (1) nitromethane, and (2) nitromethane/propanol (50:50, v/v); (b) Amylose in (1) 0·15 M KOH, (2) dimethylsulphoxide, and (3) formamide

Figures 3(a) and *3*(b) show the data for amylose acetate and amylose graphed according to (11). Again, the graphs are curved, but there is a marginal improvement in the region of low molecular weight; curvature at high molecular weights is somewhat greater than that in *Figure 2*.

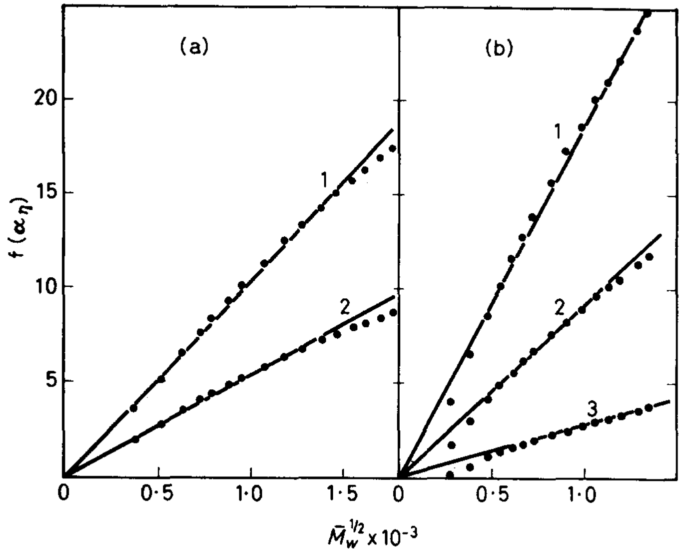

Figure 3 — Graph of $f(\alpha_\eta)$ against $\overline{M}_w^{1/2}$, where $f(\alpha_\eta) = [4{\cdot}68\,(1{\cdot}290\,\alpha_\eta^3 - 0{\cdot}290)^{2/3} - 3{\cdot}68]^{3/2} - 1$ [see equation (11) of text]: (a) Amylose acetate in (1) nitromethane, and (2) nitromethane/propanol (50:50, v/v); (b) Amylose in (1) 0·15 M KOH (2) dimethylsulphoxide, and (3) formamide

Thus the combination of (7) with (4) gives the best fit for the experimental values for amylose acetate and amylose in a variety of solvents. This is in agreement with the recent results of Ueda and Kajitani[10] obtained using poly(vinyl acetate).

COMPARISON WITH OTHER TREATMENTS OF THE EXPANSION FACTOR

The most widely used of the 'third-power law' theories is that of Stockmayer and Fixman[8] in which α_η is related to z by

$$\alpha_\eta^3 - 1 = 1{\cdot}55z \tag{12}$$

Figures 4(a) and *4*(b) show the data for amylose acetate and amylose, graphed according to (2) and (12). In *Figure 4*(a), the plot is apparently linear at low molecular weights, but curves towards the abscissa at high molecular weights. However, if equation (12) is applied to lower molecular weights [as in *Figure 4*(b)], it is obvious that the curvature is, in fact, continuous over the whole molecular weight range.. Only over a comparatively narrow range ($0{\cdot}20 \times 10^6 < \overline{M}_w < 0{\cdot}80 \times 10^6$) do the points approximate to

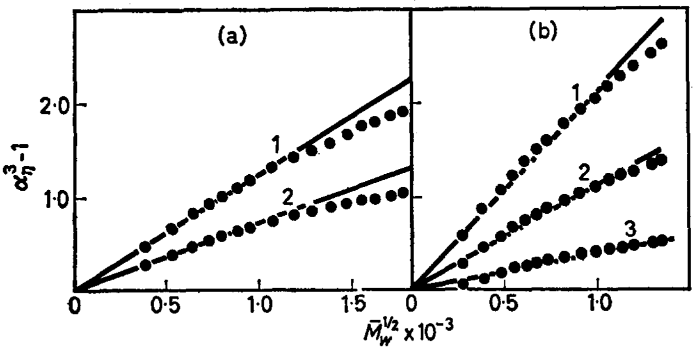

Figure 4—Graph of α_η^3-1 against $\bar{M}_w^{1/2}$ [see equation (12) of text]: (a) Amylose acetate in (1) nitromethane, and (2) nitromethane/propanol (50:50, v/v); (b) Amylose in (1) 0·15 M KOH, (2) dimethylsulphoxide, and (3) formamide

a straight line, which also passes through the origin. Thus the range of molecular weights in which (12) is approximately correct is only about half of that in which (9)–(11) are valid.

ESTIMATION OF UNPERTURBED DIMENSIONS OF THE MACROMOLECULE USING THE PTITSYN RELATION

Despite the recognized deficiencies in equation (12) this theory is widely used for determining the unperturbed dimensions of the macromolecule in solution. According to Flory

$$[\eta]=K_\theta M^{\frac{1}{2}}\alpha^3 \tag{13}$$

and

$$K_\theta=\Phi\,(\overline{r_0^2}/M)^{3/2} \tag{14}$$

where Φ is the viscosity constant. Substitution of (2) and (12) in (13) gives the Stockmayer–Fixman relation[3]

$$[\eta]/M^{\frac{1}{2}}=K_\theta+0\cdot51\ BM^{\frac{1}{2}} \tag{15}$$

Thus K_θ—and hence $\overline{r_0^2}/M$—can be determined easily from measurements carried out in good solvents. The mathematical form of (7) is not suitable for this type of manipulation. However, as first shown by Ptitsyn[4], at sufficiently high z-value, (4) may be approximated by

$$\alpha^3=[3\cdot68+(9\cdot36z)^{2/3}]/4\cdot68 \tag{16}$$

Substitution of (2) and (7) in (16) gives

$$[\eta]^{4/5}/M^{2/5}=0\cdot786\,K_\theta^{4/5}+0\cdot950\,K_\theta^{4/5}k^{2/3}M^{1/3} \tag{17}$$

where

$$k=0\cdot33\,B\,[M/\overline{r_0^2}]^{3/2} \tag{18}$$

According to (17), a graph of $[\eta]^{4/5}/M^{2/5}$ against $M^{1/3}$ should be linear with an intercept equal to 0·786 $K_\theta^{4/5}$, provided that α_η is sufficiently large.

Inagaki *et al.*[11] have suggested that the approximation is valid for $\alpha_\eta > 1{\cdot}4$. This criterion is satisfied by about half the values in the $[\eta]_4$–$\bar{M}_w$ relation for amylose. *Figure 5* shows these values graphed according to (17); reasonable linearity is observed, and extrapolation yields a value of 0·150, which gives $K_\theta = 1{\cdot}25 \times 10^{-1}$. Direct experimental determination[8] showed K_θ to be $1{\cdot}15 \times 10^{-1}$. Thus the use of (17), for $\alpha_\eta > 1{\cdot}4$, gives a value for K_θ which is only about ten per cent different from that obtained experimentally. Since this leads to an error of only about three per cent in the unperturbed dimensions, i.e. $(\overline{r_0^2}/M)^{\frac{1}{2}}$, equation (17) may be regarded as a suitable method for determining this parameter. As we have already noted, the applicability of the Stockmayer–Fixman equation is limited to a rather small range of intermediate α-values. The modified Ptitsyn relation, on the other hand, is applicable to high α-values, and hence provides a complementary analysis of viscosity–molecular weight data to that provided by the more commonly employed Stockmayer–Fixman treatment.

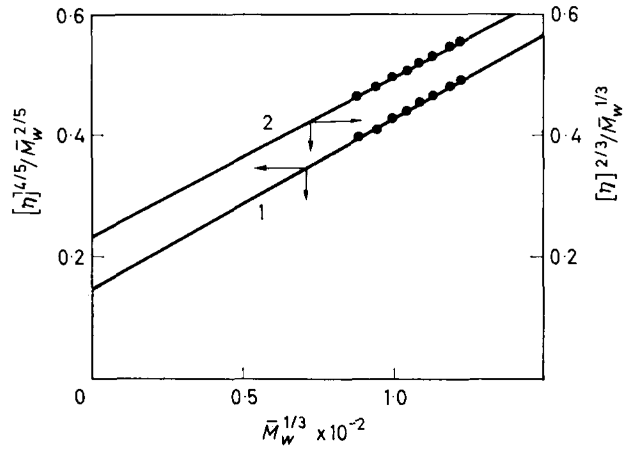

Figure 5—Graph of (1) $[\eta]^{4/5}/\bar{M}_w^{2/5}$ and (2) $[\eta]^{2/3}/\bar{M}_w^{1/3}$ against $M_w^{1/3}$ for amylose in 0·15 M KOH; $\alpha_\eta \geqslant 1{\cdot}4$

Figure 5 shows the graph obtained by combining (2), (6) and (16) which leads to

$$[\eta]^{2/3}/M^{1/3} = 0{\cdot}786\, K_\theta^{2/3} + 0{\cdot}950\, K_\theta^{2/3} k^{2/3} M^{1/3} \tag{19}$$

where k is again defined by (18). According to (19), a plot of $[\eta]^{2/3}/M^{1/3}$ as a function of $M^{1/3}$ should be linear, with an intercept of $0{\cdot}786\, K_\theta^{2/3}$. A linear relation is, in fact, observed, the intercept having a value of 0·235. This gives $K_\theta = 1{\cdot}64 \times 10^{-1}$, i.e. approximately 50 per cent greater than the experimental value. This result follows directly from the curvature at high molecular weight in *Figure 1*(b). The points corresponding to the eight highest molecular weights lie, to a reasonable approximation, on a straight line, but this line makes a positive intercept with the ordinate, rather than passing through the origin. The high value of K_θ reflects this positive intercept.

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Department of Chemistry,
The University, West Mains Road,
Edinburgh, 9, Scotland

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