Relationship of intrinsic viscosity of polymer solutions to molecular weight

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An equation derived by Han relating intrinsic visocity to molecular weight of a polymer has been fitted to experimental data over a large range of molecular weight. Excellent fits were obtained although the Mark–Houwink equation did not fit the data over the complete molecular weight range. Han's equation may be fit to intrinsic viscosity data over a moderate range of molecular weight, and is shown to then accurately predict the intrinsic viscosities for molecular weights outside this range. A method is given to compute the two parameters of Han's equation from the Mark–Houwink parameters of a polymer in a solvent.

(Keywords: intrinsic viscosity; Mark–Houwink equation; polymer solutions; polystyrene; theta solvent)

INTRODUCTION

The empirical Mark–Houwink equation, $[\eta]=KM^a$, is generally used to relate the intrinsic viscosity of a polymer at a given temperature and solvent to molecular weight. However, it applies only for a limited molecular range of molecular weight. Han[1] derived a relationship of intrinsic viscosity and molecular weight from the blob theory[2-4] of a bead-and-spring model of a polymer molecule. According to the blob theory, the internal distances in a sufficiently short polymer even in a good solvent obey Gaussian statistics so that the intrinsic viscosity is of the form:

$$[\eta]_0=K_0M^{1/2} \tag{1}$$

for molecular weights less than a given molecular weight, M_1. For larger molecular weights, the intrinsic viscosity increases more rapidly with molecular weight. Using relationships for the radius of gyration and the hydrodynamic radius of a polymer and a dynamical argument of Weill and Cloizeaux[5], Han derives an equation for intrinsic viscosity that may be written as[6]:

$$[\eta]/[\eta]_0=F(M/M_1) \tag{2a}$$

where the function

$$F(M/M_1)=1 \quad \text{for } M<M_1 \tag{2b}$$

and

$$\begin{aligned}F(M/M_1)=4/3x^{1/2}\{&x^{-2}(3-2/x)+6x^{1/5}[5/11(1-x^{-11/5})\\&-5/16(1-x^{-16/5})]\}/\{2(1-1/3x)\\&+5/2(x^{2/5}-1)-5/7(x^{2/5}-x^{-1})\}\end{aligned} \tag{2c}$$

for $M>M_1$, where $x=M/M_1$.

This relationship is shown in *Figure 1*.

FITTING TO EXPERIMENTAL RESULTS

In order to compare Equation (2) with measurements of intrinsic volume, Han assumed that the solvent and temperature dependence of the number of monomers per statistical segment, the statistical length, and the K value at theta conditions, K_0, was negligible. He used the value of K, 0.085 ml g^{-1}, at the theta temperature, 34.5°C, of polystyrene for K_0. The value of M_1 was calculated by Equation (12) of Ref. 1 using values obtained from analysis of measurements of radii of gyration of polystyrene in benzene. Thus he compared Equation (2) with measurements of intrinsic viscosity of polystyrene in benzene and cyclohexane. The agreement was impressive considering that no adjustable parameters were used, although the deviations were considerably larger than the errors of the intrinsic viscosity measurements.

In this paper, K_0 and M_1 are treated as adjustable parameters and the intrinsic viscosities of polystyrene in a variety of solvents are fitted. By Equations (1) and (2a):

$$[\eta]=K_0M^{1/2}F(M/M_1) \tag{3}$$

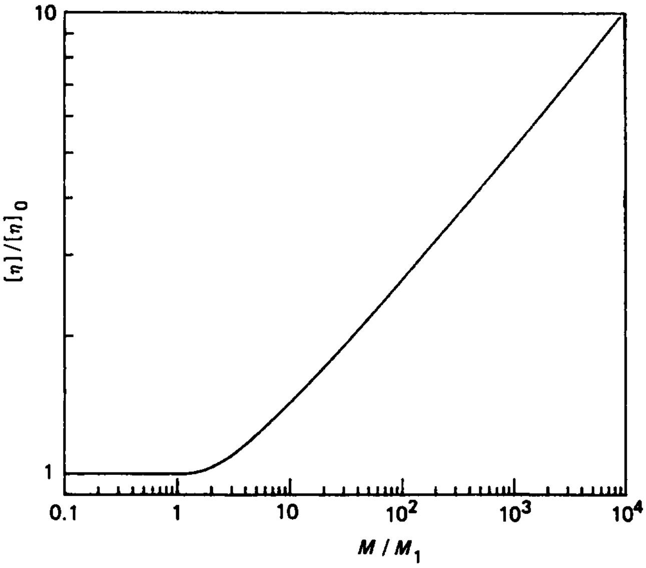

Figure 1 Han's relationship of intrinsic viscosity *versus* molecular weight

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Values of K_0 and M_1 were determined for a number of polymers and solvents by fitting Equation (3) to their intrinsic viscosities; the fitting was performed by a standard non-linear least-squares computer program. *Figure 2* shows measurements of the intrinsic viscosity of polystyrene in toluene collected from eight different papers by Herman Wagner[7] for which the molecular weights were determined by absolute methods. The molecular weights range from 660 to 4×10^6. Over this range of molecular weights, the logarithm of intrinsic viscosity *versus* logarithm of molecular weight is not a linear function so the Mark–Houwink equation does not fit the data. However, Equation (2), plotted as a solid curve, gives an excellent fit. *Figure 3* shows intrinsic viscosities *versus* molecular weight of polystyrene in benzene (Wagner[7]) and the fit by Equation (2). Equation (2) is seen to also give an excellent fit for this system.

The intrinsic viscosity of polystyrene in cyclohexane is of special interest. At 34.5°C, cyclohexane is a theta solvent for polystyrene with $K = 0.0857$ ml g^{-1} so that the parameters for Equation (1) are $K_0 = 0.0857$ ml g^{-1} and M_1 = infinity. For increasing temperatures, cyclohexane becomes a better solvent for polystyrene so that M_1 should decrease. Also the polymer will expand even at molecular weights less than M_1, so that K_0 should increase. *Figure 4* shows the fit of Equation (1) for intrinsic viscosities of polystyrene in cyclohexane at 45, 50 and 55°C (data from Refs 8, 9 and 8, respectively). The expected behaviour for M_1 and K_0 is observed, although the data for 50°C appear anomalous.

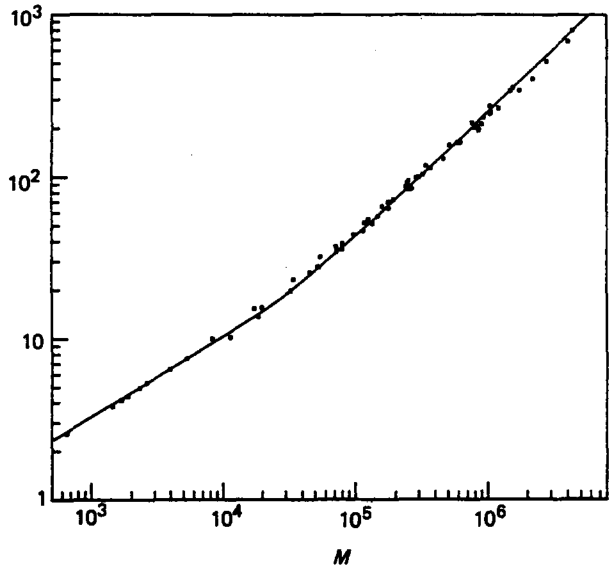

Figure 2 Measurements of the intrinsic viscosity of polystyrene in toluene from Ref. 7. Han's equation with $K_0 = 0.1033$ and $M_1 = 14\,000$ is shown by the line

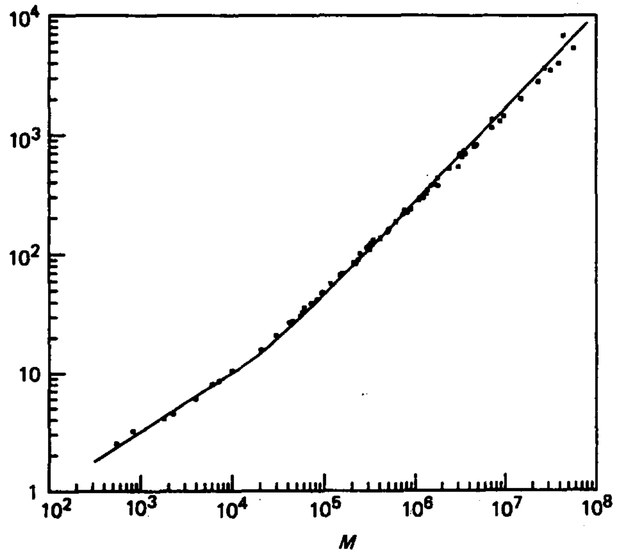

Figure 3 Measurements of the intrinsic viscosity of polystyrene in benzene from Ref. 7. Han's equation with $K_0 = 0.1002$ and $M_1 = 9200$ is shown by the line

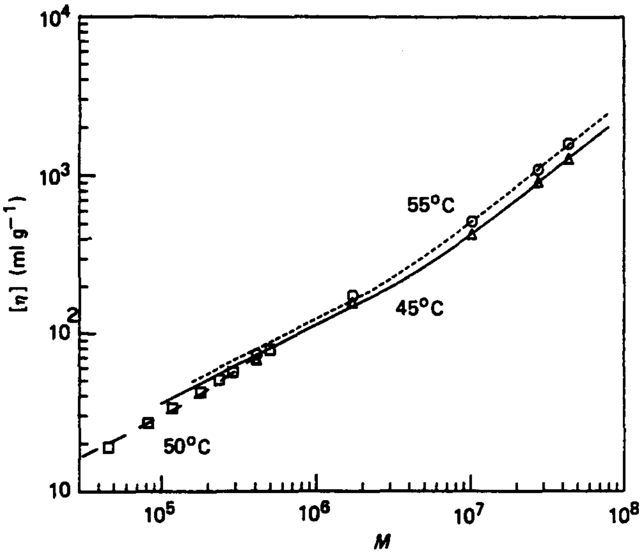

Figure 4 Measurements[8,9] of intrinsic viscosities of polystyrene in cyclohexane at 45, 50 and 55°C. Han's equation for: Δ, 45°C, $K_0 = 0.1134$, $M_1 = 2.24 \times 10^6$; □, 50°C, $K_0 = 0.0940$, $M_1 = 9 \times 10^4$; ○, 55°C, $K_0 = 0.1242$, $M_1 = 1.5 \times 10^6$ are shown by the lines

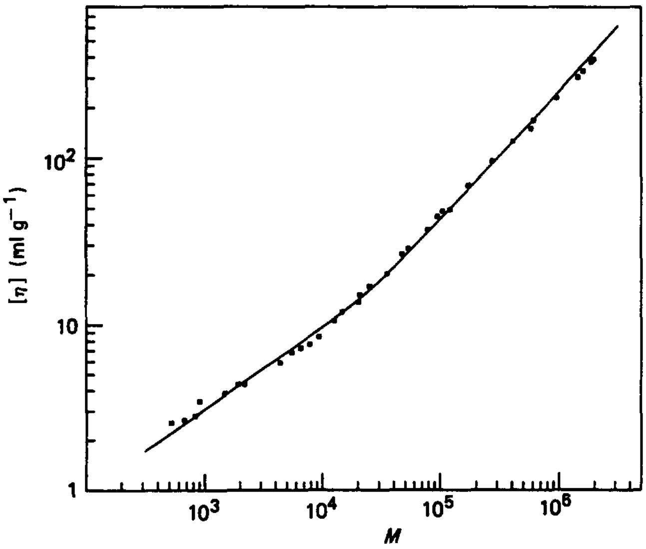

Figure 5 Measurements[10] of intrinsic viscosity of polystyrene in tetrahydrofuran. Han's equation with $K_0 = 0.0968$ and $M_1 = 11\,000$ is shown by the line

Unfortunately, measurements over the complete molecular weight range at a single temperature are not available so an exact test of Han's equation cannot be made. The extrapolations of the fits for 45 and 55°C to lower molecular weights give larger intrinsic viscosities than those measured for 50°C so Han's equation may not apply for polystyrene in the poor solvent cyclohexane. More experimental measurements are required to provide a definitive answer.

Figure 5 shows intrinsic viscosities of polystyrene in tetrahydrofuran and the fit by Equation (2). A good fit is obtained, although there are some deviations of points from the curve, especially at low molecular weights.

Figures 6 and *7* show intrinsic viscosities of poly(methyl methacrylate) in toluene and benzene and their fit to Equation (2). Again, good fits are obtained.

Because Equations (1) and (2) contain only two adjustable constants, the model may be fitted with data over a moderate range of molecular weights. In order to test whether the model will then correctly predict values outside the range of molecular weights used for the fit, Equation (2) was fitted to the intrinsic viscosity data of *Figure 2* using only the points with molecular weights in the range 10^4 to 10^6. The resulting curve is compared with the data in *Figure 8*. The intrinsic viscosities outside the fitted range are seen to be accurately predicted by Equation (2).

RELATION TO MARK–HOUWINK COEFFICIENTS

The parameters K_0 and M_1 may be calculated from the parameters K and a obtained by fitted intrinsic viscosities to the Mark–Houwink equation over a moderate range of molecular weights. We have from the Mark–Houwink equation:

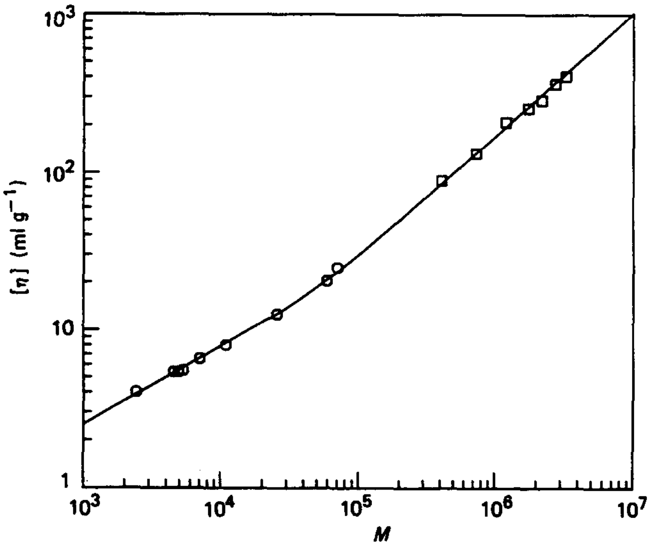

Figure 6 Measurements[11,12] of intrinsic viscosity of poly(methyl methacrylate) in toluene. Han's equation with $K_0=0.07885$ and $M_1=21\,400$ is shown by the line

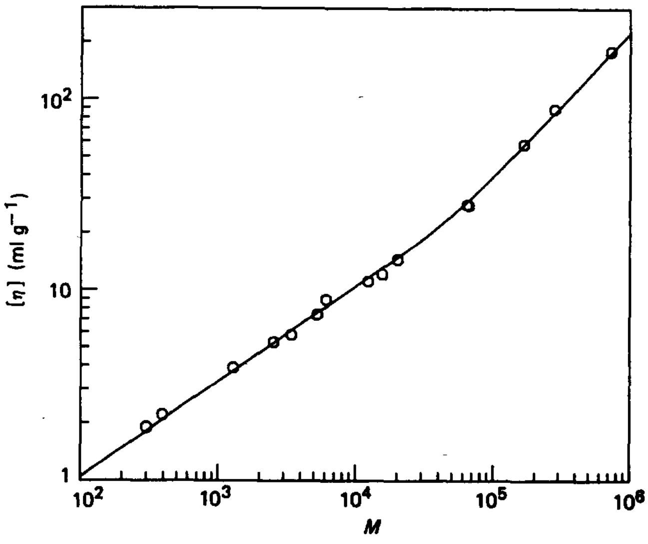

Figure 7 Measurements[13] of intrinsic viscosity of poly(methyl methacrylate) in benzene. Han's equation with $K_0=0.1046$ and $M_1=20900$ is shown by the line

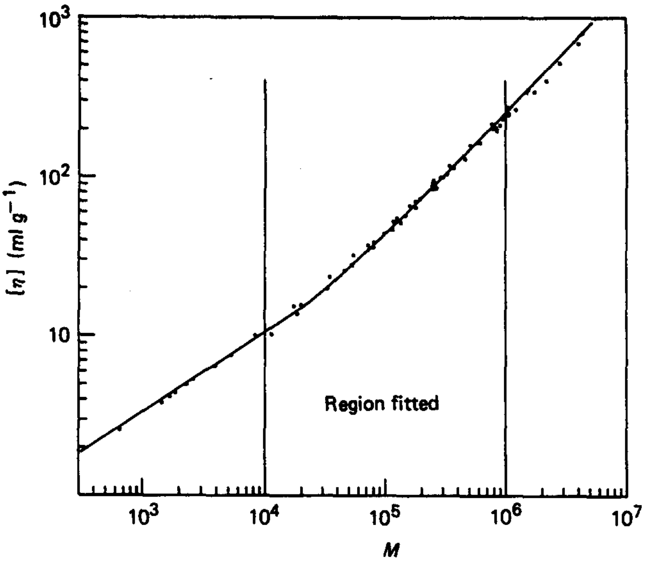

Figure 8 Measurements of intrinsic viscosity of polystyrene in toluene shown in *Figure 2*. The data was fit to Han's equation using only intrinsic viscosities for molecular weights between 10^4 and 10^6 giving $K_0=0.1051$ and $M_1=14\,000$. Han's equation with these parameters is shown by the solid line and is seen to predict accurately the intrinsic viscosity for molecular weights higher and lower than the range fitted

$$\frac{\mathrm{d}\log[\eta]}{\mathrm{d}\log M}=a \qquad (4)$$

From Equations (1) and (2):

$$\frac{\mathrm{d}\log[\eta]}{\mathrm{d}\log M}=\frac{1}{2}+\frac{M/M_1}{F(M/M_1)}\,\frac{\mathrm{d}F(M/M_1)}{\mathrm{d}\,(M/M_1)} \qquad (5)$$

so that

$$a=\frac{1}{2}+\frac{M/M_1}{F(M/M_1)}\,\frac{\mathrm{d}F(M/M_1)}{\mathrm{d}\,(M/M_1)} \qquad (6)$$

The right-hand side of Equation (6) is given in *Table 1 versus* M/M_1. The value of M/M_1 corresponding to the value of a may be found from this table. Then, using a value for M in the middle of the range of molecular weights used to fit the Mark–Houwink equation, the value of M_1 is determined. Because the molecular weights used cover several decades, it is suggested that the root-mean-square $M=(M_{\min}M_{\max})^{1/2}$ be used instead of the mean, where $M_{\min}$ and $M_{\max}$ are the minimum and maximum values of molecular weights of points used in fitting the Mark–Houwink equation. The value of K_0 is then given by:

$$K_0=\frac{[\eta]}{M^{1/2}F(M/M_1)} \qquad (7)$$

derived from Equations (1) and (2). The value of $F(M/M_1)$ is also given in *Table 1*. Thus, the parameters M_1 and K_0 are determined from the Mark–Houwink parameters K and a.

DISCUSSION AND CONCLUSIONS

Accurate measurements of intrinsic viscosity are available over a sufficiently large molecular weight range to test Han's equation for only five systems. For these systems

Table 1 Relationship between the Mark–Houwink parameter a and the parameter M_1 of Han's equation

a by Equation (7)	M/M_1	$F(M/M_1)$
0.50	<1	1
0.51	1.149	1.0005
0.52	1.230	1.0015
0.53	1.302	1.0029
0.54	1.373	1.0048
0.55	1.444	1.0070
0.56	1.516	1.0098
0.57	1.593	1.013
0.58	1.673	1.017
0.59	1.759	1.021
0.60	1.851	1.026
0.61	1.952	1.032
0.62	2.064	1.038
0.63	2.188	1.046
0.64	2.327	1.055
0.65	2.486	1.065
0.66	2.670	1.077
0.67	2.887	1.091
0.68	3.147	1.108
0.69	3.468	1.127
0.70	3.873	1.152
0.71	4.409	1.183
0.72	5.145	1.223
0.73	6.227	1.277
0.74	7.945	1.352
0.75	10.980	1.464
0.76	17.134	1.640
0.77	32.278	1.939
0.78	83.4	2.52
0.79	446	4.07
0.80	∞	∞

Han's equation with only two adjustable constants gave excellent fits while the Mark–Houwink equation did not fit over the large molecular weight range. The parameters K_0 and M_1 may be accurately fitted to intrinsic viscosities over a moderate range of molecular weight, then intrinsic viscosities may be predicted for molecular weights outside the range. This extrapolation is shown to be accurate for one example.

A method is given for easily determining K_0 and M_1 from the Mark–Houwink parameter of a polymer–solvent system.

It would be desirable to test Han's equation for other polymer–solvent systems to determine if it *universally* applies to all systems. This requires intrinsic viscosity measurements for polymers of very low and very high molecular weights.

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REFERENCES

1 Han, C. C. *Polymer* 1979, **20**, 1083

2 Farnoux, B., Boue, F., Cotton, J. P., Daoud, M., Jannink, G., Nierlick, M. and DeGennes, P. G. *J. Phys.* 1978, **39**, 77

3 Daoud, M. Thesis, Universitè de Paris VI, 1977

4 Farnoux, B. *Ann. Phys.* 1976, **1**, 73

5 Weill, G. and des Cloizeaux, J. *J. Phys.* 1979, **40**, 99

6 Han refers to number of segments, N in polymer and number of segments, N_τ, which separates Gaussian and excluded volume regions. This paper refers to molecular weights. We have $M/M_1 = N/N_\tau$

7 Wagner, H. L. *J. Phys. Chem. Ref. Data* 1985, **14**, 1101

8 Slagowski, E. L. Thesis, University of Akron, 1972

9 Papaxian, L. A. *Polymer* 1969, **10**, 399

10 American Polymer Standards Corporation, 'Catalog of Polymer Standards for Research and Development', P.O. Box 901, Mentor, Ohio 44061-0901

11 Patrone, E. and Bianchi, U. *Macromol. Chem.* 1966, **94**, 52

12 Chinai, S. N., Matlak, J. D., Resnick, A. L. and Samuels, R.^{2}J. *J. Polym. Sci.* 1955, **17**, 391

13 Fox, T. G., Kinsinger, J. B., Mason, H. F. and Schuele, E. M. *Polymer* 1962, **3**, 71