

$$b_x'' = 3b_x^0 \left\{ \left(1 + \frac{3}{2}\alpha_{sh} - \frac{m\alpha_{sh}}{2} \right) - 2(1 + \alpha_{sh})K \times \left[\frac{1 + \frac{2}{3} \left(\frac{-2 - 2\alpha_{sh} + k_s\alpha_{sh} + 2k_s}{1 + \alpha_{sh}} \right) \beta}{1 - \beta} \right] + K^2 \left[\frac{1 - 3 \left(\frac{1}{2} - \frac{k_s}{2} + \frac{k_s^2}{6} \right) \beta}{1 - \beta} \right] \right\} \quad (73)$$

The β in eq. 71-73 is defined by the equation

$$\beta = \frac{n_r k_s k_\sigma}{\sigma_2'} \quad (74)$$

It is possible that some of the quantities assumed in the foregoing derivations to be independent of temperature do in fact vary with the temperature. If so, appropriate adjustments must be made in these relationships.

The functions deduced for χ_h and ψ_s show a very similar dependence on concentration. (Compare eq. 28 with eq. 59, also 31 with 62 and 32 with 63). Therefore χ_h and χ_s should vary oppositely, a behavior that has often been noted empirically. In certain systems the relationship is approximately a rectilinear one.^{7,12,13} The accuracy of the rectilinearity probably depends on the magnitudes of certain of the parameters.

Correlation with Experiment

From precise experimental data one can determine χ and its dependence on concentration and temperature, hence values of ψ_a^0 , b_x^0 , and the ratios ψ_a'/ψ^0 , ψ_a''/ψ_a^0 , b_x'/b_x^0 , and b_x''/b_x^0 . If β is negligible, one

(12) H. Takenaka, *J. Polymer Sci.*, **24**, 321 (1957).

(13) G. Rehage and H. Meys, *ibid.*, **30**, 271 (1958).

can use these ratios and eq. 68, 69, 72, and 73 (putting $\beta = 0$) to deduce the remaining four unknowns in these equations: K , α_{sh} , k_s , and m . From eq. 35, one can obtain k_{sh} . Equation 12 will then give f_{sh} as a function of the concentration. Equation 67 will yield n_r and eq. 71 will give α_L (assuming that α_s has been estimated by means of eq. 5). From K and k_{sh} , one can (eq. 33) determine the product $k_{ext}k_{ms}$, but not the individual values of these two factors. Likewise, from eq. 34, one can obtain the product $\sigma_2'\Delta\epsilon$, but not σ_2' and $\Delta\epsilon$ separately.

In this way, one can determine, from experimental data, all the constants needed for substitution into the closed-form equations for $\Delta\bar{H}_1$ and $\Delta\bar{S}_1$ (eq. 28 and 54).

If β is not negligible, the more complicated equations, containing this quantity, must be used; another experimental quantity, such as ψ_a'''/ψ_a^0 or b_x'''/b_x^0 , is needed, unless one or more of the "unknowns" can be determined or estimated in another way.

Testing of the equations presented in this paper, using published experimental data, has been begun. The results will be reported in due course. If the theory and its equations should prove satisfactory, it will be possible, from a relatively small amount of experimental data, to deduce curves for the variation of the thermodynamic properties of polymer solutions up to quite high concentrations. (At very high concentrations certain other factors⁶ not considered in the present development may become important.) It is hoped, moreover, that the theory will lead to the determination of the various molecular constants which affect the thermodynamic solution properties and so eventually to a better understanding of the phenomena and an ability to predict the properties of new systems.

An extension of this theory to solutions of graft and block copolymers has already been published.¹⁴

(14) M. L. Huggins, *ibid.*, **C1**, 445 (1963).

[CONTRIBUTION FROM THE MELLON INSTITUTE, PITTSBURGH 13, PENNSYLVANIA]

Viscometric Tests of Excluded Volume Theories

BY G. C. BERRY AND T. G. FOX

RECEIVED APRIL 15, 1964

Some aspects of viscometric tests for excluded volume theories are discussed. Attention is confined to those systems for which the intrinsic viscosity and the molecular weight are known, possibly as a function of temperature. It is concluded that definitive evaluation of the various theories requires data at higher molecular weights than normally studied or over a large temperature span.

Introduction

It is our purpose here to comment briefly on some aspects of viscometric tests for the various theories of the excluded volume effect in polymer coils. We will restrict our attention to studies for which *only* $[\eta]$ and M are known, possibly as a function of temperature. Viscometric studies have recently received renewed interest because of new theoretical developments in both the hydrodynamic and thermodynamic aspects of the problem. It is an over-simplification to consider these aspects separately, but the theoretical developments which attempt to include both effects simultaneously are still at an early stage.¹⁻³

(1) M. Kurata and H. Yamakawa, *J. Chem. Phys.*, **29**, 311 (1958).

(2) O. B. Ptitsyn and I. E. Eizner, *Zh. Fiz. Khim.*, **32**, 2464 (1958).

Thermodynamic Effects on the Intrinsic Viscosity

The molecular description of the hydrodynamic flow has been understood in terms of equivalent models advanced by Debye and Bueche,⁴ Kirkwood and Riseman,⁵ and others,^{6,7} and this description has been utilized to form the basis of approximations to include thermodynamic (excluded volume) effects.^{1,2,8,9} A principle result of the hydrodynamic calculations

(3) See, for example, the review: A. Peterlin, *Makromol. Chem.*, **34**, 89 (1959).

(4) P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 565 (1948).

(5) J. G. Kirkwood and J. Riseman, *ibid.*, **16**, 565 (1948).

(6) H. C. Brinkman, *Physica*, **13**, 447 (1947).

(7) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).

(8) T. G. Fox and P. J. Flory, *J. Am. Chem. Soc.*, **73**, 1904 (1951).

(9) M. Kurata and W. H. Stockmayer, *Advan. Polymer Sci.*, **3**, 196 (1963).

is that $[\eta]$ should depend on some equivalent chain volume, at least for large enough molecular weights⁵ (more specifically for large enough h).¹⁰ It has long been recognized that the principal effect of increasing thermodynamic interaction is to augment the chain extension, and thus the equivalent volume, by some factor. Accordingly, one writes⁹

$$[\eta] = \Phi' A^3 M^{1/2} \alpha_\eta^3 \quad (1)$$

where

$$\Phi' = 6^{3/2} h F(h)$$

$$A^3 = (\bar{S}^2/M)_0^{3/2}$$

Here, the parameter h and the function $F(h)$ are left unspecified except that $hF(h)$ increases with M to within 1% of its asymptotic limit (2.89×10^{23})⁷ for $h > 3$ and that this limit is apparently reached for most flexible polymer-solvent systems, at least for $M > ca. 10^5$. The ratio of the mean-square radius \bar{S}^2 to the molecular weight M is to be taken under θ -conditions¹² (denoted by subscript 0). Equation 1 may then be considered to be a defining relation for the hydrodynamic expansion factor α_η . It should be noted that α_η is not necessarily equal to α , the expansion factor for the mean square radius.

Three expressions for α_η in terms of thermodynamic variables will be considered here. (A fourth,¹³ numerically quite close to eq. 3,¹¹ will not be discussed separately.) These are

$$\alpha_\eta^{15/p} - \alpha_\eta^{9/p} = a_1 B A^{-3} M^{1/2} \quad (2)$$

$$\alpha_\eta^{9/p} - 1 = \frac{3}{2} a_1 B A^{-3} M^{1/2} \quad (3)$$

$$\alpha_\eta^3 - 1 = 1.55 B A^{-3} M^{1/2} \quad (4)$$

where $a_1 = (134/105)$ for linear chains. The parameter B is related to the magnitude of the thermodynamic interaction and may be taken as proportional to the function $\psi_1(1 - \theta/T)$ of Flory,¹⁴ for example. Here p may be taken as 3 or $5/2$. Equation 2 with $p = 3$ is the familiar Flory-Fox⁸ equation, and is the Flory-Fox equation as modified by Kurata and Yamakawa¹ when $p = 5/2$. The difference rests on the approximation that $\alpha_\eta = \alpha$ for the former, and $\alpha_\eta^3 = \alpha^{5/2}$ for the latter. Similarly, eq. 3 results from combination of an equation due to Fixman¹⁵ for $\alpha(T, M)$ and the above mentioned approximations for α_η as a function of α . Equation 4, due to Stockmayer and Fixman,¹¹ is similar to eq. 3, but rests on a somewhat different intuitive notion.

Evaluation of Experimental Data

A. Isothermal Data.—The dependence of α_η^3 on $BA^{-3}M^{1/2}$ according to eq. 2-4 may be seen in Fig. 1. (The curves for $p = 5/2$ lie slightly below the corre-

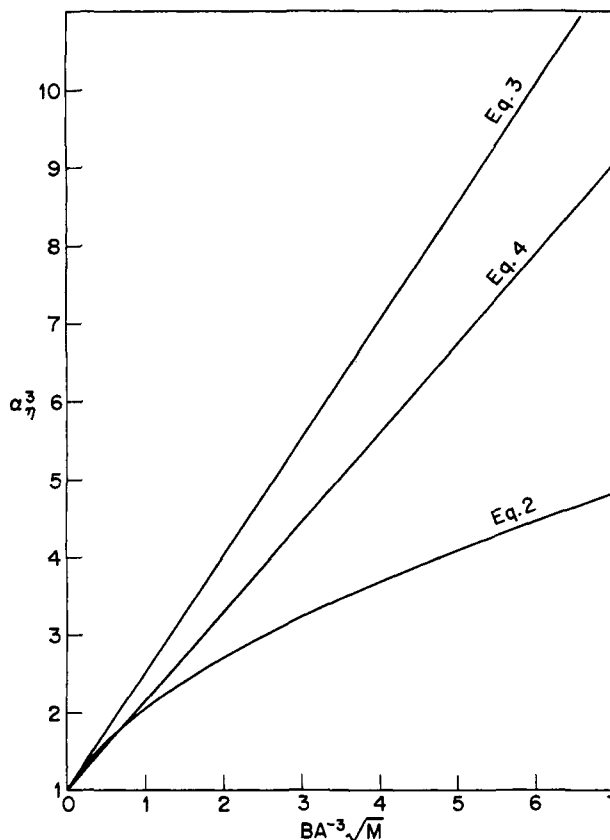


Fig. 1.—The hydrodynamic expansion factor α_η^3 vs. the thermodynamic parameter $BA^{-3}\sqrt{M}$ according to Flory-Fox (eq. 2; $p = 3$), Flory-Fox and Fixman (eq. 3; $p = 3$), and Stockmayer-Fixman (eq. 4).

sponding curves for $p = 3$ in each case.) The striking difference of the products BA^{-3} predicted by the different relations for any given α_η^3 and \sqrt{M} is apparent. Also apparent, however, is the functional similarity of the curves α_η^3 vs. $BA^{-3}\sqrt{M}$ for selected intervals of α_η^3 . For example, if experimental data are confined to the interval $2 < \alpha_\eta^3 < 5$, as in often the case for polymer with $M > 10^5$ in good solvents, then any of the curves can be represented by a relation of the form $\alpha_\eta^3 = a + mBA^{-3}\sqrt{M}$ to within a few per cent, where a and m are empirical constants. Thus, attempts to analyze the three relations on the basis of experimental α_η^3 vs. M over a restricted range of α_η require precise data if they are to succeed. For example, if in the interval $2 < \alpha_\eta^3 < 3.6$ (which corresponds to some data for polymethyl methacrylate in toluene at 60°¹⁶) eq. 2 ($p = 3$) is presumed accurate, then the values of BA^{-3} computed from eq. 4 will be constant to within $\pm 20\%$ over the same interval. A systematic error in computing BA^{-3} such as could reside in an empirical $[\eta]_0$ vs. M relation, for example, could easily cause this large a discrepancy. To be sure, estimates of BA^{-3} according to the various relations 2-4 will yield different values for BA^{-3} , but unless one has *a priori* knowledge of BA^{-3} this will not suffice to obtain the correct functional form for α_η .

Similarly, attempts to compute A^3 from viscometric data confined to systems where B is large (good sol-

(10) The notation is chosen to be consistent with recent usage.^{7,11} In particular, a definition of the hydrodynamic parameter h may be found in ref. 7.

(11) W. H. Stockmayer and M. Fixman, *J. Polymer Sci.*, **C1**, 137 (1963).

(12) P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

(13) M. Kurata, W. H. Stockmayer, and A. Roig, *ibid.*, **33**, 151 (1960).

(14) P. J. Flory, *ibid.*, **17**, 303 (1949).

(15) M. Fixman, *ibid.*, **36**, 3123 (1962).

(16) T. G. Fox, *Polymer*, **3**, 111 (1962).

vents) by extrapolation to $M = 0$ according to appropriate rearrangement of any of the above relations^{9,11,17} become suspect without *a priori* knowledge of which is the correct expression. For example, if eq. 2 ($p = 3$) is presumed correct, but the data are plotted in a manner appropriate to eq. 4,¹¹ then nearly straight lines will result until \sqrt{M} (or more correctly $BA^{-3}\sqrt{M}$) becomes small, but this line will yield too large an intercept, and hence too large a value for A^3 . This may be readily seen by examining the curve for eq. 2 in Fig. 1 over the interval $2 < \alpha_\eta^3 < 7$. A linear relation will be seen to provide reasonable fit to the data in this restricted interval (at least to within usual experimental error) but such a line will not yield $\alpha_\eta = 1$ at $BA^{-3}\sqrt{M} = 0$. Conversely, if eq. 4 is presumed correct and the data are plotted according to the format appropriate to eq. 2, then data extrapolated linearly from large values of \sqrt{M} will yield too low an intercept (too small a value for A^3). In either case, curvature is expected only when passing from high to low values of $BA^{-3}\sqrt{M}$ so that the actual shape is quite dependent on B .

Attempts to extend these treatments to lower molecular weights, where presumably the curvature mentioned above will be significant and possibly useful in deciding which is the appropriate relation to use in extrapolation, meet with another uncertainty. Inspection of values of BA^{-3} for a variety of systems over wide intervals of M , in particular at very low values of M ($< ca. 10^5$), *invariably reveals trends in BA^{-3} with M regardless of which of the eq. 2-4 is used to compute BA^{-3} .*¹⁸ This variation of BA^{-3} with M may be due to an increasing nongaussian character of the chain as M decreases, and so would not be unexpected.¹⁷

It has been found experimentally that $[\eta]_0$ is proportional to $M^{1/2}$ for $2000 \leq M \leq 4 \times 10^6$ for the system polystyrene-cyclohexane.^{19,20} This suggests that the parameter $hF(h)$ in eq. 1 has indeed attained its asymptotic value over the entire span of M . Otherwise, according to calculations of Debye and Bueche,⁴ Kirkwood and Riseman,⁵ and others,^{7,21} $[\eta]_0$ should gradually change from dependence on $M^{1/2}$ to dependence on M with decreasing M through the molecular weight dependence of $hF(h)$. Unfortunately, however, this may not be regarded as a unique conclusion. Other possibilities include dependence of B and/or A^3 on M for low M ²² or an increasing nongaussian character of the chain which has an unknown effect on the hydrodynamic equation for $[\eta]_0$. In any case, the constancy of $[\eta]_0/M^{1/2}$ together with variation of BA^{-3} with M as calculated from α_η indicates that there may be effects specific to low molecular weight polymers that have not yet been identified. In view of these uncertainties, it would seem preferable to establish first

the relation appropriate for large M before attempting to extend the treatment to vanishingly small M .

B. Temperature Dependence.—In some cases $[\eta]$ is known as a function of both molecular weight and temperature. Then, if A^3 (e.g., $[\eta]_0$), and its temperature dependence, are known as well, the value of B computed from any of eq. 2-4 may be examined to yield parameters such as Flory's ψ_1 and θ .¹⁴ In this case, B is plotted against $1/T$ and the intercept for $B = 0$ yields θ while the slope is proportional to $\psi_1\theta$. The plot should be linear^{23,24} and data for different molecular weight polymers over the same temperature interval should all superpose to yield a single curve if the correct relation is being used (see, for example, the data given in ref. 16). Unfortunately, the curves B vs. $1/T$ calculated from eq. 2-4 do not usually differ much in shape over the temperature spans normally available. Thus, evaluation rests on comparison of ψ_1 and/or θ obtained from this viscometric analysis with values obtained elsewhere, such as from light scattering or osmotic pressure studies. This type of study does seem to provide promise for eventual evaluation of eq. 2-4, but it lies outside our stated area of interest here, *viz.*, data confined to viscosity and absolute molecular weight, and so will not be pursued further here.²⁵

Mark-Houwink-Sakurada Coefficient

We now wish to examine the coefficient ν in the empirical Mark-Houwink-Sakurada equation

$$[\eta] = KM^\nu \quad (5)$$

in terms of relations 1-4. Combination of eq. 1-5 yields ν as a function of α_η for each of the eq. 2-4, denoted, respectively, by subscripts 2-4 in eq. 6-8.²⁶

$$\nu_2 = \frac{1}{2} + \frac{p}{2} \frac{\alpha_\eta^{6/p} - 1}{5\alpha_\eta^{6/p} - 3} \quad (6)$$

$$\nu_3 = \frac{1}{2} + \frac{p}{6} \frac{\alpha_\eta^{9/p} - 1}{\alpha_\eta^{9/p}} \quad (7)$$

$$\nu_4 = \frac{1}{2} + \frac{1}{2} \frac{\alpha_\eta^3 - 1}{\alpha_\eta^3} \quad (8)$$

Figure 2 shows ν as a function of α_η for the four expressions that result²⁷ (ν_4 and ν_3 ($p = 3$) are identical). The most striking difference between calculations based on Flory's¹⁴ expression for α and those based on Fixman's relation¹⁵ (or relations numerically similar¹³) is the prediction of the latter that ν should exceed *ca.* 0.75 for systems for which $\alpha_\eta \geq 1.3$, whereas the former would predict $\nu \sim 0.75$ only at much larger α_η , and in fact places an upper bound of 0.80 on ν . Typical "good solvents" have α_η in the range

(23) This assumes that the excluded volume integral has a temperature dependence given by $B_0(1 - \theta/T)$.¹⁴

(24) G. C. Berry, Preprints, Division of Polymer Chemistry, American Chemical Society, Vol. 4, No. 1, 141 (1963).

(25) G. C. B. is currently engaged in a study of this type for the system polystyrene-decalin over the temperature interval θ to $\theta + 100^\circ$. Some of the light scattering data have been given elsewhere²⁴ and these taken together with preliminary viscosity data on three molecular weight samples strongly support the predictions of eq. 2.

(26) Specifically, $\nu = (1/2) + (d \ln \alpha_\eta^3 / d \ln M)$. It is assumed explicitly that ν and K are independent of molecular weight. Thus, α_η in eq. 6-8 is to be viewed as an average value for the molecular weight span used to determine ν .

(27) We here assume that $\partial hF(h) / \partial M$ can be neglected.

(17) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1952.

(18) Early investigations, as well as later studies, have consistently shown that BA^{-3} computed from viscometric data according to the Flory-Fox relations exhibits a continuous decrease with decreasing M for M below some value characteristic of a given system.¹⁷ Examination of these same data according to eq. 4 of Stockmayer and Fixman, for example, reveals a continuous increase in BA^{-3} with decreasing M for M in the range where the discrepancy with the Flory-Fox relations is noted.

(19) T. Altares, D. P. Wyman, and V. R. Allen, *J. Polymer Sci.*, in press.

(20) W. R. Krigbaum and P. J. Flory, *ibid.*, **11**, 37 (1953).

(21) J. E. Hearst, *J. Chem. Phys.*, **37**, 2547 (1962).

(22) In particular, the Flory θ -temperature, which is included in B , should depend on M for very low M .

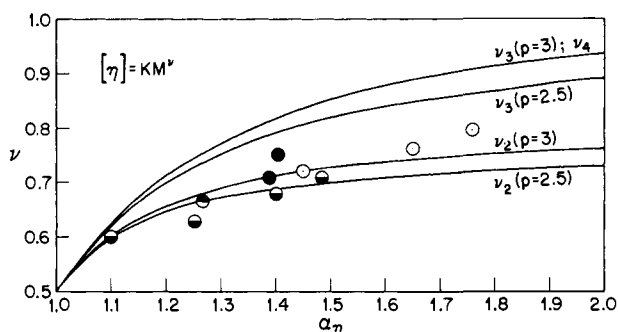


Fig. 2.—Coefficient ν ($[\eta] = KM^\nu$) vs. α_η according to the equations indicated and for some experimental data (see Table I). Polymers (see Table I): polymethyl methacrylate \circ ; polyisobutylene \odot ; polystyrene \bullet ; polyvinyl acetate \bullet .

1.2–1.7 for $M > 10^6$. Some representative values of ν given in Table I have been plotted vs. a mean value of α_η .²⁸ The latter is taken as the mean value of α_η in the span covered to determine ν . Admittedly, it would be better to plot ν vs. α_η for each data point, but experimental accuracy seldom permits this.

TABLE I				
Polymer	Solvent	α_η^a	ν	Ref.
Methyl methacrylate	Chloroform	3.1–7.9	0.80	<i>a</i>
Methyl methacrylate	Dichloroethane	4.4–5.3	0.76	<i>a</i>
Methyl methacrylate	Methyl methacrylate	2.8–3.5	0.72	<i>a</i>
Styrene	Toluene	1.4–3.5	0.71	<i>b</i>
Styrene	Benzene	1.5–3.5	0.75	19
Isobutylene	Benzene	1.6–2.5	0.66	<i>c</i>
Vinyl acetate	Butanone	2.6–3.5	0.71	<i>d</i>
Vinyl acetate	Benzene	2.2–3.2	0.67	<i>e</i>
Vinyl acetate	Trichlorobenzene	1.7–2.2	0.62	<i>e</i>
Vinyl acetate	Methanol	1.3–0.4	0.60	<i>f</i>

^a E. Cohn-Ginsberg, T. G. Fox, and H. F. Mason, *Polymer*, **3**, 97 (1962). ^b P. Outer, C. I. Carr, and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950). ^c T. G. Fox and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949). ^d R. O. Howard, Doctoral Thesis, Massachusetts Institute of Technology, 1952; and A. R. Schultz, *J. Am. Chem. Soc.*, **76**, 3422 (1954). ^e G. C. Berry, L. M. Hobbs, and V. C. Long, *Polymer*, **5**, 31 (1964). ^f M. Matsumoto and Y. Ohyanagi, *J. Polymer Sci.*, **46**, 441 (1960).

The experimental values are seen to favor eq. 2, but not unequivocally so. A few points at higher α_η would clearly be useful since this is where the largest difference in the predicted values for ν appears. It should be emphasized that values of $\nu > 0.75$ are expected according to eq. 3 and 4 whenever $\alpha > 1.5$, regardless of what the value of B might be. Clearly, however, the larger B the smaller M is predicted to be for the appearance of $\nu > 0.75$. Data in the usual systems apparently require fairly large M ($>$ say 10^6) for α_η to be greater than about 1.8. This means that experimental determination of ν becomes difficult for a variety of reasons, including imprecise measurement of M for very large M ($> 10^7$), fairly large shear corrections to $[\eta]$, which decrease the measured values of $[\eta]$ as M increases, thus yielding too low values for ν ,

(28) Several examples of systems for which ν is near unity given by Kurata and Stockmayer⁹ have been omitted from Fig. 2 since values of ν quoted for these systems vary widely. (See M. M. Huque, D. A. I. Goring, and S. G. Mason, *Can. J. Chem.*, **36**, 952 (1958); A. M. Holtzer, H. Benoit, and P. Doty, *J. Phys. Chem.*, **58**, 624 (1954).) In addition, these are systems for which the polymer is normally considered to behave as a stiff chain and the analysis required is beyond our scope here.

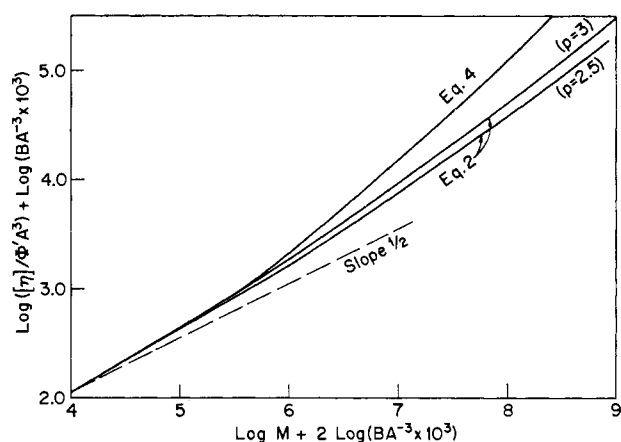


Fig. 3.—A reduced plot of $[\eta]/\Phi'A^3$ vs. M .

and possible polymer degradation for large values of M .²⁹

The variation of α_η with temperature discussed above also is reflected in a dependence of ν on temperature; and, provided a large enough temperature interval can be spanned, this dependence can also be utilized to evaluate eq. 6–8.

The experimental observation that ν tends to 0.5 in good solvents as M decreases is in accord with any of eq. 6–8 if the molecular weight dependence of $hF(h)$ may be ignored and gaussian statistics assumed to be valid. A considerable body of experimental data does in fact exhibit this type of behavior (see, for example, ref. 9 or 19). The molecular weight M^* for which ν becomes 0.5 (to within experimental error) depends of course on the product BA^{-3} , M^* increasing as BA^{-3} decreases. The nature of the expected transition may be seen in Fig. 3. Here a reduced plot of $[\eta]$ vs. M is constructed for each of the equations 1, 2 and 4. It is seen that the transition occurs over a narrow enough span in M to allow a very large span in M to be correlated by two expressions of the Mark-Houwink-Sakurada type with two different sets of constants K and ν , K and ν changing at some molecular weight M^* which depends on BA^{-3} (the transition occurs for $BA^{-3}\sqrt{M^*}$ ca. unity).

Figure 3 may be useful in itself to obtain an estimate for B if A^3 is known (from measurement of $[\eta]_0/\sqrt{M}$ for example). It could serve as a master curve for comparison of $[\eta]/\Phi'A^3$ vs. M with one of the theoretical relations to obtain BA^{-3} and hence B . Thus, the graph of the experimental data is shifted relative to the master curve, Fig. 3 (two units of horizontal shift for every one unit of vertical shift), to obtain BA^{-3} as the shift factor required for coincidence of the two graphs. This method has the advantage of allowing one to obtain a simultaneous fit of all of the data by inspection.

Equations 1–4 may also be used to obtain an estimate of K and ν simultaneously from a single determination of $[\eta]$ and M in a good solvent provided A^3 is known. This subject has been discussed more extensively by

(29) A low shear rate viscometer has been constructed according to the design of Zimm and Crothers, in connection with a study on which one of us (G.C.B.) is currently engaged, and it will probably be used to study some high molecular weight polymers (ca. 10^7) in a number of good solvents for which extensive investigation at lower molecular weights has been performed in an effort to determine ν at large α_η : B. H. Zimm and D. M. Crothers, *Proc. Natl. Acad. Sci.*, **48**, 905 (1962).

Orofino and Fox.³⁰ (Equation 6 ($p = 3$) was also obtained by these authors.)

Conclusion

In summary, we are forced to conclude that no definitive evidence for the unique applicability of any of the eq. 2-4 has yet been exhibited on the basis of combined viscometric and absolute molecular weight data alone. This inadequacy may be traced directly to failure of any of the theories to describe adequately the data for low molecular weight ($M < 10^5$) systems. This uncertainty makes analysis of data restricted to good solvents to determine the thermodynamic parameter B and/or the chain extension parameter A^3 hazardous since the values obtained depend directly on the extrapolation procedure employed which in turn depends on which of the eq. 2-4 are used.

Similarly, attempts to extrapolate $[\eta]$ vs. M correlations to molecular weights higher than those explicitly studied are liable to yield erroneous results unless the correct set of relations is used. That is, any of the relations 2-4 could very well fit a given set of data in a good solvent over a restricted molecular weight

(30) T. A. Orofino and T. G. Fox, Aeronautical Systems Division Report ASD-TR 61-22, Part I, United States Air Force, Wright-Patterson Air Force Base, Ohio.

range (with a different value of BA^{-3} for each relation to be sure) with acceptable precision, but still yield quite different correlations at higher (or lower) molecular weights. Indeed, $[\eta]$ - M data on the system polystyrene-benzene¹⁹ correlate with either eq. 2 ($p = 5/2$) or with eq. 4 with about the same precision over the molecular weight span $10^4 < M < 2 \times 10^6$, although the values of BA^{-3} so obtained differ by a factor of 3. These calculated $[\eta]$ vs. M curves differ considerably, however, by the time M is ca. 10^7 .

It is suggested that the most reliable evaluation of viscosity-molecular weight relationships may involve examination of $[\eta]$ - M data as a function of temperature for systems where there is *a priori* knowledge of the thermodynamic parameter B (as well as A^3) as a function of temperature, that is, knowledge of ψ_1 and θ . Further, it is suggested that examination of the Mark-Houwink-Sakurada coefficient ν at high molecular weight (high α_η) should provide a basis for a reasonable choice between at least some of the relations 2-4.

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[CONTRIBUTION FROM THE PLASTICS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC., WILMINGTON, DELAWARE]

The Molecular Structure of Polyethylene. XV. Comparison of Number-Average Molecular Weights by Various Methods¹

By F. W. BILLMEYER, JR., AND V. KOKLE

RECEIVED APRIL 2, 1964

Number-average molecular weight was determined for samples of both linear and branched polyethylenes by at least two of the thermodynamic methods of osmometry, cryoscopy, and ebulliometry, the kinetic method of thermoelectric differential vapor pressure, and the chemical method of end-group analysis. Within the known limitations of each technique, the agreement among methods was excellent, the results of three different methods often falling within a range of less than 5%.

Introduction

Measurement of the molecular weight of high polymers has been a subject of great scientific and technological importance ever since the macromolecular nature of these compounds was proved in the early 1920's. Very few new techniques for these measurements have been developed since that time, however, the latest of these with a thermodynamic basis being the light scattering method of Debye² yielding information on particle size as well as the weight-average molecular weight and second virial coefficient. More recently, a kinetic method has been proposed³ for the determination of the number-average molecular weight, and several older techniques have been improved or applied for the first time to random-coil polymers.

This paper considers several methods for determining the number-average molecular weight in application

at elevated temperature to branched and linear polyethylene. These techniques include osmometry, cryoscopy (as described in paper XIII of this series⁴) and ebulliometry,⁵ the above-mentioned thermoelectric differential vapor pressure method,³ and the chemical method of end-group analysis by infrared spectroscopy. The purpose of this research was to define the range of applicability of each of the above methods and to demonstrate the validity of the results of kinetic and chemical methods in application to the polyethylene system. This involves comparisons among the results of the various methods; other comparisons of this type were presented in paper XI of this series⁶ for number-average molecular weights determined by osmometry and cryoscopy and in paper XIV⁷ for weight-average molecular weights determined by light scattering and by Archibald ultracentrifugation.

(1) Previous papers in this series are published in *J. Am. Chem. Soc.*, **75**, 6110 (1953); **79**, 5079 (1957); **81**, 3219 (1959); *J. Polymer Sci.*, **62**, 251 (1961); **A1**, 1921 (1963); and an article in press; and *J. Phys. Chem.*, **67**, 2728 (1963).

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