Dilute Solution Properties of Narrow-distribution Polystyrene

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An experimental study of the dilute solution properties of several narrow-distribution polystyrenes ($5 < 10^{-4}M < 50$) is described. Theoretical relationships correlating A_2, $\langle M \rangle_w$, and $[\eta]$ are examined for data obtained in both a thermodynamically good and poor solvent. The empirical $[\eta]/M$ relation obtained in toluene has been compared with published data and, in some cases, large variations were found between the calculated and known viscosity-average molecular weights. It has been demonstrated that Krigbaum's semi-empirical equation provides the closest fit for all the data. One also concludes that the original Flory–Krigbaum–Orofino expression overestimates the expansion factor, α. In this molecular weight range, the simple $[\eta]/M$ relationship due to Stockmayer and Fixman is shown to allow a good estimation of the unperturbed dimensions, $\langle S^2 \rangle_0/M$, while the entropy parameter, ψ_1, appears to be too low.

ALTHOUGH the dilute solution properties of polymers have been studied extensively for many years, some of these investigations have involved materials having ill-defined distributions in molecular weight. Since most theories of dilute polymer solutions assume the use of 'monodisperse' samples, it is evident that conclusions based upon such results could be misleading. The advent of recent techniques in the anionic polymerization of styrene, for example, provides the polymer chemist with relatively narrow-distribution samples required for such investigations. Furthermore, recent theoretical developments concerning the dilute solution properties of linear macromolecules have generated renewed interest in this area and consequently require detailed experimental support using current refinements in technique and instrumentation.

It is the purpose of this study to determine accurately the dilute solution properties of several of these polystyrene samples and to analyse their properties with respect to current theories of polymer solutions. As part of a longer range effort in this area, it is hoped that this experimental study will help to establish relationships useful in the interpretation of data on stereoregular polymers and thus provide a more quantitative means for their characterization.

EXPERIMENTAL DETAILS

Materials

All polystyrene samples used in this study were prepared by the anionic polymerization of styrene and are therefore expected to have a narrow distribution of molecular weights. Five of these samples were supplied through the courtesy of the late Dr H. C. McCormick of The Dow Chemical Company. Two samples, C1 and C2, were synthesized in this laboratory by Dr C. Geacintov. The solvents, cyclohexane (M.C.C.: technical grade) and toluene (M.C.B.: reagent grade) were freshly purified by distillation through a Vigreaux column packed with glass beads; only the constant-boiling centre fractions were used.

Viscometry

The viscosity measurements were performed with Cannon–Ubbelohde dilution viscometers having flow times greater than 150 seconds. In both solvent systems, the highest molecular weight sample, S1159, exhibited Newtonian behaviour, as determined with a variable-shear capillary viscometer; a similar observation with the same sample has been reported by Cowie and co-workers[1]. No kinetic energy corrections have been applied.

Data for the seven polystyrene samples were obtained in toluene at 25·0°C and in cyclohexane at 50·0°C. In each case, intrinsic viscosities, $[\eta]$, were obtained from the common intercept of plots of $\eta_{sp.}/c$ and $(\ln \eta_{rel.})/c$ versus concentration (in g/100 ml of solution) according to the relationships

$$\eta_{sp.}/c = [\eta] + k'[\eta]^2 c \tag{1}$$

and

$$(\ln \eta_{rel.})/c = [\eta] - k''[\eta]^2 c \tag{2}$$

where k' is the Huggins constant and $k' + k'' = \frac{1}{2}$. For the toluene data, the average value of k' for seven samples was $0{\cdot}35 \pm 0{\cdot}07$, and generally the sum of k' and k'' was close to 0·5. For the same system, McCormick[2] found no significant variation in k' with molecular weight in this range and one calculates an average value of $0{\cdot}35 \pm 0{\cdot}02$. The average value of k' in cyclohexane at 50°C was found to be $0{\cdot}46 \pm 0{\cdot}06$; recent results in 'poor' solvent systems by Orofino and Mickey[3] support this observed trend in k'.

Table 1. Intrinsic viscosity results

	$[\eta]$, *dl/g*			$[\eta]$, *dl/g*	
Sample	*in toluene, 25°C**	*in cyclohexane, 50°C*	*Sample*	*in toluene, 25°C**	*in cyclohexane, 50°C*
S1159	1·58 (1·59)	0·78$_5$	S103	0·52$_2$ (0·525)	0·33$_5$
C-1	0·99$_3$	0·56$_5$	S102	0·38$_8$ (0·379)	0·27$_0$
S108	0·87$_3$ (0·86)	0·50$_5$	C-3	0·25$_6$	0·19$_0$
NBS705	0·70$_1$	0·42$_3$			

*Values in parentheses reported by Cowie *et al.*[1].

Table 1 contains the intrinsic viscosities obtained for the various samples in these two solvents. In addition, data reported by Cowie and co-workers[1] for four of the same samples are included for comparison. It is apparent that the agreement between laboratories is good.

Light scattering

A Brice–Phoenix photometer[4] (1000 series) was used for all light scattering measurements with unpolarized light of 436 nm wavelength. Angular measurements were possible through the use of the small slit system and large cylindrical cells blackened with optically flat paint to minimize stray surface reflections. The overall alignment of the optical system and cell was ensured by using dilute, filtered fluorescein solutions; in the angular range $30° \leqslant \theta \leqslant 135°$, the variation of the observed fluorescence (after correction for the volume of solution viewed by the photomultiplier tube) was found to be less than one per cent. For maintaining constant temperature, silicon oil was passed through a cylindrical housing[5] by a Haake circulator using short insulated conduits; this arrangement was estimated to provide temperature control to better than one centigrade degree (at 50°C) within the light scattering cell.

All solutions and sols in this study were carefully clarified by repeated passage through inert Millipore filters[6] of 0·22 μm pore size. These filters were tightly clamped into a stainless steel holder for which specially designed heating mantles were made. Reproducible scattering data and essentially ideally clarified systems were obtainable by cycling the sols and solutions three times through the filter unit (with slight filtered nitrogen pressure) and the light scattering cell. All equipment (cells, syringes etc.) for this important clarification step was first thoroughly cleansed by vapours of the solvent to be used.

The instrument was calibrated with Ludox sols (colloidal silica supplied by E. I. duPont de Nemours) whose turbidities were directly measured with a Cary model 14 spectrophotometer using 10 cm cells. These sols were diluted with 0·05 M potassium chloride solutions for improving stability and reproducibility[7]; proper precautions (e.g. blackened cells and small apertures) were also taken for minimizing forward secondary scattering and stray reflections[8, 9]. The turbidity and light scattering data ($\theta = 90°$) obtained with the same sols were extrapolated by least squares to infinite dilution according to the method suggested by Kraut and Dandliker[10]. Using the calibration constant obtained by this treatment and the refractive index correction of Hermans and Levinson[11], the Rayleigh ratio ($R_{90°}$) for spectro-quality filtered benzene was found to be $46{\cdot}4 \times 10^{-6}$ cm^{-1} ($\pm 0{\cdot}5$ per cent) at $\lambda = 436$ nm and room temperature. This value agrees very well with the suggested value ($R_{90°} \lesssim 45{\cdot}6 \times 10^{-6}$ cm^{-1}) of Kratohvil and co-workers[7, 12, 13] and also with a value of $46{\cdot}8 \times 10^{-6}$ cm^{-1} determined more recently by Jennings and Jerrard[14].

Further assurance of the reliability of this calibration procedure and the derived constants was possible by using a polystyrene sample (NBS705) currently available from the National Bureau of Standards. The weight-average molecular weight of this sample, as determined from light scattering measurements in cyclohexane at 50°C, was found to be $1{\cdot}7_9 \times 10^5$ (± 2 per cent, the average deviation of two runs), in perfect agreement with the quoted value. It should be noted that the method of calibration for the NBS instrument[15] is based upon geometrical optics rather than Ludox sols. The constancy of the photometer optics, response and calibration was periodically checked by measuring the transverse scattering of benzene sealed in a square cell; this observed scattering has remained essentially unchanged over the past three years.

Refractive index differences were measured by means of a modified Brice–Speiser differential refractometer[16] calibrated with dilute aqueous potassium chloride solutions[17]. The modifications include replacing the original cell holder with a larger one in order to obtain better temperature uniformity across the cell; consequently a more stable and well-defined image of the slit was possible for operation at higher temperatures. In addition, the cell was aligned in contact with two stainless steel plates having rectangular holes for passage of the light beam. (Indeed, more recent measurements at 145°C have been quite successful.) To minimize solvent evaporation, the original glass penny-head stoppers were abandoned in favour of tapered Teflon plugs. The overall reproducibility was further improved by (1) mounting a chin rest on the instrument, and (2) installing a set of dial indicators near the cell housing. All measurements for a given determination were performed by three operators and the results averaged.

For the polystyrene–cyclohexane system at 50°C, the average value of the refractive index increment for several determinations was 0·188 ml/g at $\lambda = 436$ nm. This value is in good agreement with analogous results of O'Mara and McIntyre[18] and also Notley and Debye[19].

For each sample, duplicate light scattering measurements were performed at eleven angles of observation (from $\theta = 135°$ to $\theta = 35°$ from the forward direction of the incident beam) and at five concentrations (generally less than one per cent). These data, programmed for the 1410 IBM computer*, were treated according to the familiar equation[20]

$$Kc/R_\theta = 1/\langle M\rangle_w P(\theta) + 2A_2'c \qquad (3)$$

where R_θ is Rayleigh's ratio at the angle of observation θ, c the polymer concentration in g/ml of solution, A_2' the second virial coefficient† in cm³-mole/g², $P(\theta)$ the particle scattering function, and K is the constant containing the square of the refractive index increment. It is generally found that plots of Kc/R_θ against $[\sin^2(\theta/2) + kc]$, where k is an arbitrary constant, produce a gridlike linear graph.

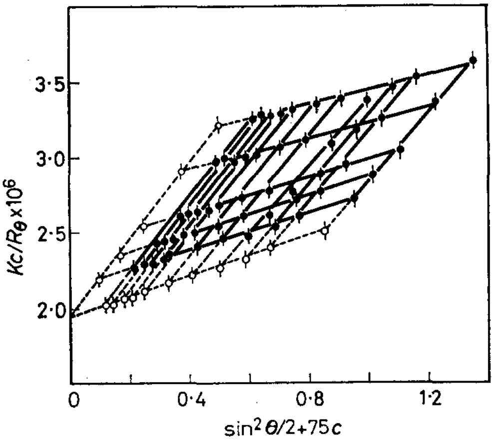

Figure 1—Zimm plot for S1159 in cyclohexane at 50°C

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*This computer programme includes a least squares analysis of the data, programmed by Mr C. Cotterill of the Socony Mobil Computer-Communications Department; when justified, this extension enhances the accuracy of the required extrapolations.

†For convenience, the second virial coefficient obtained from light scattering is denoted by the primed quantity, A_2', while that derived from osmometry is given the usual notation, A_2. Under the same conditions, these parameters are identical, as will be shown later.

Table 2. Osmometry and light scattering data

Sample	$10^{-5}\langle M\rangle_w$*	$10^5 A_2'$ (*cm*^{3}*-mole/g*^{2}, *in cyclohexane*)	$10^{-5}\langle M\rangle_n$	$10^4 A_2$ (*cm*^{3}*-mole/g*^{2}, *in toluene*)	$\frac{\langle M\rangle_w}{\langle M\rangle_n}$
S1159	$5{\cdot}1_3$ (4·95)	$9{\cdot}5_0$	$4{\cdot}1_8$	$4{\cdot}5_4$	$1{\cdot}2_2$
C–1	$2{\cdot}8_7$	$8{\cdot}7_4$	$2{\cdot}8_5$	$4{\cdot}5_1$	$1{\cdot}0_1$
S108	$2{\cdot}4_2$ (2·30)	$10{\cdot}_2$	$2{\cdot}3_6$	$4{\cdot}6_0$	$1{\cdot}0_2$
NBS705	$1{\cdot}7_9$	$9{\cdot}6_7$	$1{\cdot}6_4$	$4{\cdot}7_5$	$1{\cdot}0_9$
S103	$1{\cdot}1_7$ (1·20)	$11{\cdot}_3$	$1{\cdot}0_6$	$4{\cdot}9_5$	$1{\cdot}1_0$
S102	$0{\cdot}80_2$ (0·84)	$10{\cdot}_6$	$0{\cdot}74_3$ (0·795)	$5{\cdot}7_5$	$1{\cdot}0_8$
C–3	$0{\cdot}45_9$	$12{\cdot}_9$	$0{\cdot}37_6$	$5{\cdot}8_8$	$1{\cdot}2_3$

*Values in parentheses reported by Cowie *et al.*[1].

Figure 1 illustrates such a 'Zimm plot' obtained for a polystyrene sample (S1159) in cyclohexane at 50°C. The weight-average molecular weight, $\langle M\rangle_w$, is derived from the reciprocal of the common intercept of the zero concentration and zero angle lines; the second virial coefficient, A_2', is obtained from the slope of the latter line, since $P(0)=1$ by definition. The average values of $\langle M\rangle_w$ and A_2' are listed in *Table 2* which also summarizes the analogous results obtained by osmometry.

Osmometry

Osmotic pressure determinations were performed with the Stabin–Shell automatic osmometer[21] using gel cellophane (type '600') membranes obtained from J. V. Stabin and Company, Jamaica, New York. Solvent asymmetry values were ascertained prior to and after all solution measurements; in general, such a procedure yielded asymmetries easily reproducible to better than 0·02 cm.

The validity of these measurements can, to some extent, be estimated from data obtained with the NBS705 polystyrene sample. For nine different solutions of this sample in toluene at 50°C, a linear relationship between

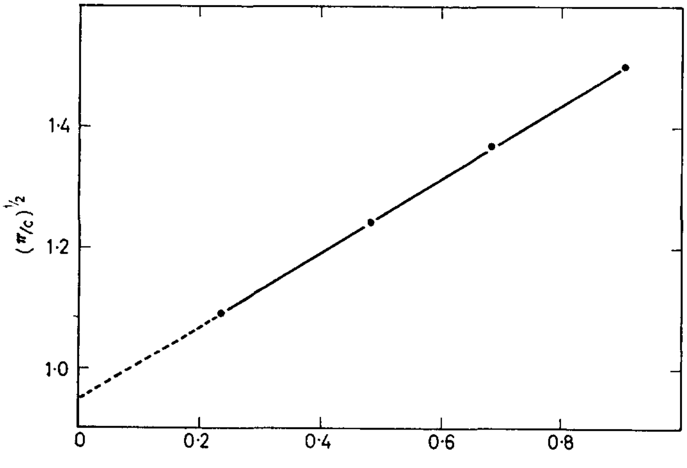

Figure 2—Osmotic plot for C–1 in toluene at 30°C

$(\pi/c)^{\frac{1}{2}}$ and c was observed; a least squares analysis of these data yields $\langle M\rangle_n = 1{\cdot}6_7 \times 10^5$, in excellent agreement with the quoted value of $1{\cdot}7_0 \times 10^5$.

For each sample, the osmotic pressure determinations were performed at four (or more) concentrations in distilled toluene at 30·0°C. These data were treated (by least squares analysis) according to the familiar relationship

$$(\pi/c)^{\frac{1}{2}} = (\pi/c)_0^{\frac{1}{2}}\,[1 + (\Gamma_2/2)\,c] \qquad (4)$$

where π is the osmotic pressure in g/cm^2 and $\Gamma_2 = A_2\langle M\rangle_n$. Linear relationships between $(\pi/c)^{\frac{1}{2}}$ and c were obtained, as illustrated by *Figure 2* for sample C – 1. Number-average molecular weights, $\langle M\rangle_n[=RT/(\pi/c)_0]$, and second virial coefficients, A_2, were calculated from the slopes and intercepts of such plots.

DATA ANALYSES

The experimental results in *Table 2* indicate that the molecular weight distributions of these samples are quite narrow ($\langle M\rangle_w/\langle M\rangle_n \sim 1{\cdot}1$, for most samples); for this reason, it is possible to utilize such data with existing theories of polymer solution behaviour assuming 'monodisperse' samples.

Mark–Houwink–Sakadura (MHS) relationships

This section concerns the analysis of the intrinsic viscosity data and the weight-average molecular weights derived from light scattering measurements; these relationships are then compared with published data.

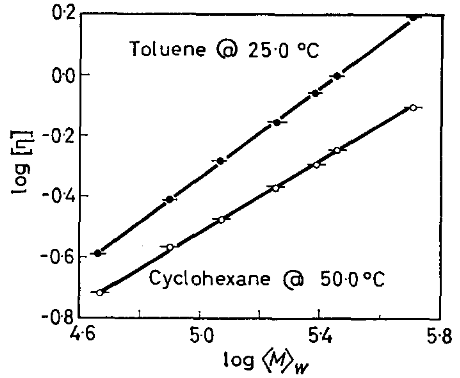

Figure 3—Molecular weight dependence of the intrinsic viscosity

Figure 3 shows the customary $\log[\eta]/\log\langle M\rangle_w$ plots representing the empirical relation

$$[\eta] = K'M^{\nu} \qquad (5)$$

where K' and ν are considered as constants for a given system within a limited range of molecular weight. For the polystyrene–toluene system at 25·0°C, the data yield

$$[\eta] = 8{\cdot}4_8 \times 10^{-5}\langle M\rangle_w^{0{\cdot}74_8} \qquad (6)$$

by linear least squares analysis. (All linear relationships have been treated in this manner.) It is interesting to note that these constants are only slightly affected by the exclusion of any set of $[\eta]/\langle M\rangle_w$ values; specifically, the value of ν varies by less than one per cent.

Similarly, one obtains

$$[\eta]=3{\cdot}6_4\times10^{-4}\langle M\rangle_w^{0{\cdot}58_4} \tag{7}$$

for polystyrene in cyclohexane at 50·0°C. It has been established that the θ-temperature for a polystyrene–cyclohexane system[22, 23] is very close to 34°C, and that under such conditions, where there are no net interactions between polymer and solvent, $\nu=0{\cdot}50$. It is therefore not surprising to find that $\nu=0{\cdot}58$ for this system.

The relatively narrow molecular weight distributions of these samples allow one to evaluate critically the many published values[1, 24-34] of K' and ν for the polystyrene–toluene system at 25°C and 30°C. For an observed intrinsic viscosity, a corresponding viscosity-average molecular weight, $\langle M\rangle_v$, was calculated using published values of K' and ν. This derived $\langle M\rangle_v$ value must lie between $\langle M\rangle_n$ and $\langle M\rangle_w$ and should be closer to $\langle M\rangle_w$. In some instances, such calculations for several samples yielded $\langle M\rangle_v$ greater than $\langle M\rangle_w$ by as much as 15 to 45 per cent; in all cases, however, $\langle M\rangle_v$ values were greater than $\langle M\rangle_n$ as expected. The main reasons for such large variations are believed to be uncertainties in calibration and the use of unfractionated samples. Among the twelve relationships considered, only four provided good correlation with the present data; in particular, the unique data of Cowie *et al.*[1] should be mentioned since the samples used have been *shown* to be relatively 'monodisperse'. Fortunately, these workers have actually studied four of the same samples considered here; the measured values of $\langle M\rangle_w$ and $\langle M\rangle_n$ all agree within experimental error (see *Table 2*). This analysis merely emphasizes the need for careful selection of various published MHS parameters. It is surprising to find that such variations exist in the literature for this system.

For a later discussion, it is especially important to examine, in a similar manner, the extensive work of Krigbaum and Flory[35]. Their osmometry data on several sharp fractions of polystyrene were used to established a MHS relationship in benzene at 25°C. Through the use of viscosity data obtained using the same samples in benzene and toluene[25], the desired relationship for toluene is readily obtained; this relationship also yields $\langle M\rangle_v$ values within the expected range.

Estimations of the unperturbed dimensions of polystyrene

This section concerns the application of intrinsic viscosity molecular weight data for obtaining K (or K_θ) in the familiar Fox–Flory equation

$$[\eta]=KM^{\frac{1}{2}}\alpha^3 \tag{8}$$

By definition,

$$K=6^{3/2}\,\Phi\,(\langle S^2\rangle_0/M)^{3/2} \tag{9}$$

and

$$\alpha^2=\langle S^2\rangle/\langle S^2\rangle_0 \tag{10}$$

where Φ was first considered to be a constant ($\sim 2{\cdot}1\times10^{23}$ in c.g.s. units);

$\langle S^2\rangle^{\frac{1}{2}}$ and $\langle S^2\rangle_0^{\frac{1}{2}}$ denote the root-mean-square radius of gyration of a linear macromolecule in solution and under theta conditions respectively. Under theta conditions, Φ becomes $\Phi_0 \cong 2{\cdot}8 \times 10^{23}$ and $K = K_\theta$; then, it is well known that

$$[\eta]_\theta = K_\theta M^{\frac{1}{2}} \tag{11}$$

However, in some cases (e.g. crystalline polymers), such measurements are not feasible, and consequently, one needs to know the dependence of α on M. A few methods proposed for obtaining K (or K_θ) from $[\eta]/M$ data alone will be considered here.

Krigbaum and Flory's[35] data on polystyrene in cyclohexane provide an excellent basis for this test. Under theta conditions for this polymer–solvent system ($\theta = 34°C$), they obtained an average value of $K_\theta = 8{\cdot}2 \times 10^{-4}$ for eleven fractionated samples of polystyrene. More recently, Altares, Wyman and Allen[36] have also found that, for many polystyrene samples having $\langle M\rangle_w \sim \langle M\rangle_n$, $K_\theta = 8{\cdot}4\,(\pm 0{\cdot}2) \times 10^{-4}$ in cyclohexane at 34·5°C. Furthermore, it is important to note that these data cover a rather *large* range in molecular weight ($800 < M < 2 \times 10^6$).

Fox–Flory–Schaefgen (*FFS*) *method*

The early theoretical treatment of Flory[37,38] leads to the relation

$$\alpha^5 - \alpha^3 = 2C_M\,(\tfrac{1}{2} - \chi_1)\,M^{\frac{1}{2}} \tag{12}$$

with

$$C_M = (27/2^{5/2}\pi^{3/2})\,(\bar{v}^2/N_A V_1)\,(6\langle S^2\rangle_0/M)^{-3/2} \tag{13}$$

where $\bar{v}$ is the partial specific volume of polymer, V_1 is the molecular volume of the solvent, N_A is Avogadro's number, and χ_1 is the polymer–solvent interaction parameter.

It can be shown that equations (8) and (12) yield[39]

$$[\eta]^{2/3}/M^{1/3} = K^{2/3} + 2C_M\,(\tfrac{1}{2} - \chi_1)\,K^{5/3}\,(M/[\eta]) \tag{14}$$

indicating that the intercept of a plot of $[\eta]^{2/3}/M^{1/3}$ against $M/[\eta]$ should allow one to obtain K. However, data extrapolated to $(M/[\eta]) = 0$, obtained in both 'good' and 'poor' solvent systems for a given polymer, do not always yield a common intercept†. *Figure 4* represents such a plot where the underestimation of K is apparent. The analysis yields $K = 3{\cdot}2_6 \times 10^{-4}$ in toluene and $K = 8{\cdot}0_5 \times 10^{-4}$ in cyclohexane. Therefore, equation (14), although still used indiscriminately by some investigators, appears to be limited to estimations of K in 'poor' solvent systems.

The difference between K and K_θ may be attributed to a solvent effect upon Φ. According to Ptitsyn and Eizner[41]

$$\Phi = \Phi_0\,(1 - 2{\cdot}63\epsilon + 2{\cdot}86\epsilon^2) \tag{15}$$

where ϵ is related to the MHS exponent ν through the relationship

$$\nu = (1 + 3\epsilon)/2 \tag{16}$$

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†Stockmayer[40] has suggested theoretically that a factor of 0·4913 be included into the RHS of equation (12); it is apparent that the incorporation of this factor does not alter the conclusions presented here.

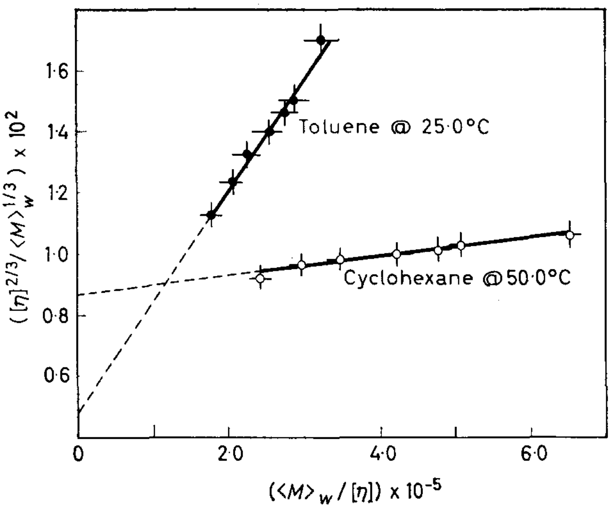

Figure 4—Viscosity plot for Fox–Flory–Shaefgen method

If one therefore considers this influence of solvent upon the K value derived from the toluene data, its value would only increase to $K_\theta = 5{\cdot}0 \times 10^{-4}$.

Kurata–Stockmayer (KS) procedure

In a very extensive publication, Kurata and Stockmayer[42] proposed a new method for obtaining the unperturbed dimensions of linear macromolecules from $[\eta]/M$ data. This approach utilizes a slight modification of an equation due to Kurata, Stockmayer and Roig[43] who assumed an ellipsoidal model for the polymer molecule. The basic equations are:

$$\alpha_\eta^3 - \alpha_\eta = 1{\cdot}10\, g(\alpha_\eta)\, z \tag{17}$$

where

$$g(\alpha_\eta) = 8\alpha_\eta^3/(3\alpha_\eta^2 + 1)^{3/2} \tag{18}$$

with

$$z = (3/2\pi)^{3/2} B A^{-3} M^{1/2} \tag{19}$$

and

$$A^2 = 6\,\langle S^2\rangle_0/M \tag{20}$$

where B is related to the solute–solvent interaction parameter χ_1.

In addition, one *now* takes

$$[\eta] = K_\theta M^{1/2} \alpha_\eta^3 \tag{21}$$

as the defining expression for α_η, the viscosity expansion factor. These equations yield

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0{\cdot}363\, \Phi_\theta B\, [g(\alpha_\eta)\, M^{2/3}/[\eta]^{1/3}] \tag{22}$$

from which a first approximation of K_θ is obtained by plotting $[\eta]^{2/3}/M^{1/3}$ against $M^{2/3}/[\eta]^{1/3}$; then, one evaluates the necessary expressions for $[\eta]_\theta$, α_η and $g(\alpha_\eta)$ and replots according to (22). This procedure has been shown to result in a common intercept for good and poor solvent data for many systems[42].

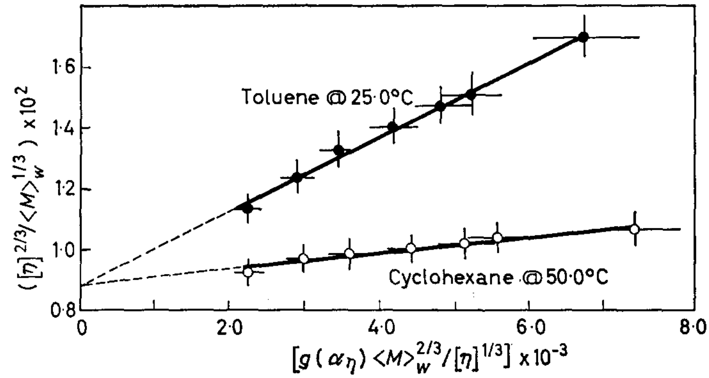

Figure 5—Viscosity plot for Kurata–Stockmayer–Fixman method

The application of this method to the present data is illustrated in *Figure 5*. One obtains $K_\theta = 8{\cdot}2_3 \times 10^{-4}$ in toluene and $K_\theta = 8{\cdot}3_2 \times 10^{-4}$ in cyclohexane, both in very good agreement with the 'directly measured' value of $8{\cdot}2 \times 10^{-4}$. The only disadvantages of this method are the lengthy procedure and inconvenient form of the equations used; nevertheless, it is clear that the method works quite well independent of the solvents used here for the viscosity measurements.

It is interesting that the entropy parameter, ψ_1, can also be estimated from data plotted according to equation (22). From the slope of this plot, one obtains the polymer–solvent parameter[38], B, given by

$$B = 2\bar{v}^2(1-\theta/T)\psi_1/V_1N_A \qquad (23)$$

Such a calculation is encouraging for the polystyrene–cyclohexane system since the variation of ψ_1 values derived by various methods is yet to be explained[44]. If one assumes that $\Phi_0 = 2{\cdot}5 \times 10^{21}$*, $\bar{v} = 0{\cdot}935$ ml/g[45], $\theta = 307{\cdot}4\,°K$[22,23] and $V_1 = 1{\cdot}22 \times 10^2$ cm^3/mole, one obtains a value of $\psi_1 = 0{\cdot}22$. Such agreement with some recent estimations may appear reasonable. For example, the osmotic pressure measurements of Krigbaum and Geyer[46] indicate $\psi_1 = 0{\cdot}23$ while Fujita *et al.*[47] obtain $\psi_1 = 0{\cdot}19$ from sedimentation–equilibrium experiments. Other determinations are 0·36 and 0·38 from osmometry[22,3] and 1·06 from precipitation temperature measurements[48]. However, it will be shown later that ψ_1 obtained from such plots may be too low.

Stockmayer–Fixman (SF) method

More recently, Stockmayer and Fixman[49] have proposed another equation for estimating the parameter K_θ from viscosity–molecular weight data. In this approach, earlier equations developed by Fixman[50] and Kurata and Yamakawa[51] lead them to conclude that

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*This value is assumed to account for the slight polydispersity in all these samples[41].

$$\alpha_\eta^3 = 1 + 1{\cdot}55\,z \tag{24}$$

which surprisingly agrees numerically with equation (17)*. It is easily shown that equation (24) (referred to here as the SF equation) and equation (21) lead to the very simple relationship

$$[\eta] = K_\theta M^{\frac{1}{2}} + 0{\cdot}51\,\Phi_\theta B M \tag{25}$$

This equation clearly separates the effects of short- and long-range interactions into two separate terms and is similar in form to a semi-empirical equation suggested earlier by Burchard[52] and Krigbaum[53] (to be considered later).

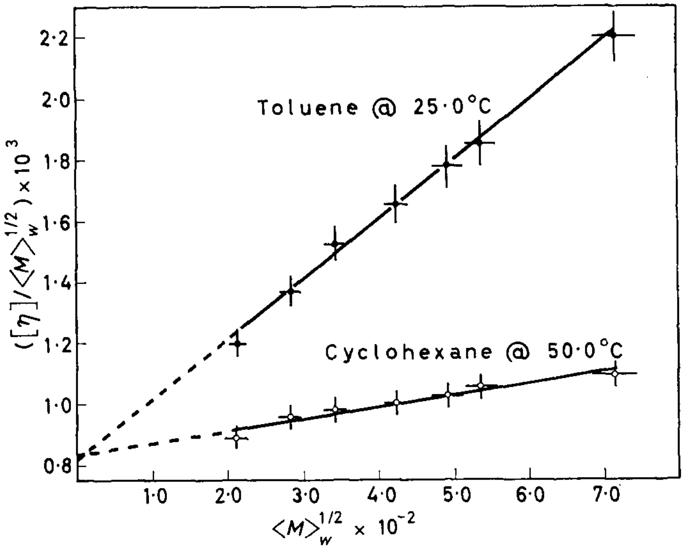

Figure 6—Viscosity plot for Stockmayer–Fixman method

The application of this method is illustrated in *Figure 6*, for both solvent systems. The linearity and common intercept for both systems is supporting evidence for equation (25): furthermore, the data analysis yields $K_\theta = 8{\cdot}1_5 \times 10^{-4}$ for the toluene data and $8{\cdot}3_0 \times 10^{-4}$ with cyclohexane as the solvent. As with the KS approach, excellent agreement with the 'direct measured' value of K_θ in addition to the existence of a common intercept for both solvent media implies that these equations describe the dilute solution properties of many polymer–solvent systems; of course the present method is preferred due to its simplicity. As outlined before, one can also obtain an estimation of the entropy parameter, ψ_1, from the slope of $[\eta]/M^{\frac{1}{2}}$ versus $M^{\frac{1}{2}}$ plots; assuming $\Phi_0 = 2{\cdot}5 \times 10^{21}$ for the cyclohexane system, one

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*This agreement is further apparent upon considering the dependence of α_η^3 on z. Such a plot for equation (17) is *essentially* linear; however, an expression for $S = \mathrm{d}\alpha_\eta^3/\mathrm{d}z$ can be derived. This slope rises to a maximum value ($\sim$ 1·76) near $\alpha_\eta = 1{\cdot}5$ and thereafter approaches a limiting value of 1·69 at sufficiently high α_η. In contrast, equation (24) predicts $S = 1{\cdot}55$ for all α_η.

finds $\psi_1 = 0{\cdot}24$, again in fair agreement with some of the other determinations discussed previously.

As Kurata and Stockmayer[42] have suggested, it is interesting to calculate the intrinsic viscosity–molecular weight dependence, as predicted by both the KS and SF methods. For the toluene system, the polymer–solvent interaction parameters B, obtained from each analysis, have been utilized; it is also assumed that $\Phi_0 = 2{\cdot}5 \times 10^{21}$, and $K_\theta = 8{\cdot}2 \times 10^{-4}$.

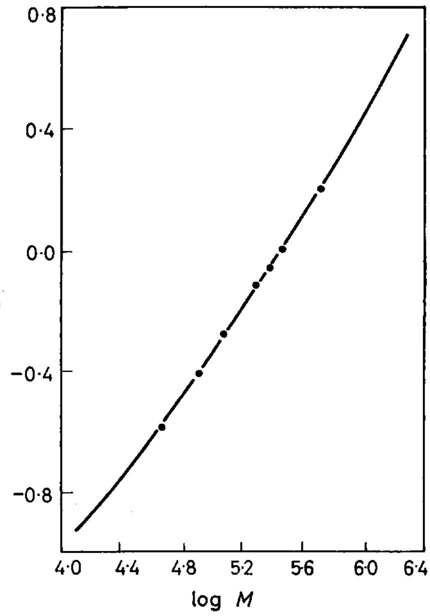

Figure 7—Viscosity–molecular weight relation for polystyrene in toluene at 25 °C, according to equations (22) and (25)

These latter parameters allow one to calculate z through use of equations (17), (18), (19) and (24). The necessary α_η^3 parameters are then obtained from the corresponding graph of α_η^3 against z. One finally calculates the intrinsic viscosity, at a predetermined molecular weight, from equation (21). *Figure 7* illustrates the molecular weight dependence of the intrinsic viscosities calculated by this method. The solid curve represents this calculated variation for *both* the KS and SF treatments; the darkened circles illustrate the experimental data using intrinsic viscosities and weight-average molecular weights. It is apparent that such an analysis shows excellent agreement with experiment on a log/log plot.

Okada, Toyoshima and Fujita[54] have briefly mentioned that an equation of the form

$$\alpha^3 = 1 + A_1 M^{\frac{1}{2}} + \mathrm{O}\,(M) \tag{26}$$

where A_1 is a constant, can be obtained by a series expansion of equation (17) in the region of low M. Since this equation is quite similar to the SF relationship, this interrelationship was examined in more detail. Upon expansion of equation (17), one obtains

$$\alpha_\eta^3 = 1 + 3/2\, h(\alpha_\eta)\, z + \,..\, 3/2\,(3/2-1)\,..\,(3/2-i+1)\,[h(\alpha_\eta)\, z]^i / i! \tag{27}$$

with

$$h(\alpha_\eta) = 8{\cdot}80\, \alpha_\eta / (3\alpha_\eta^2 + 1)^{3/2} \tag{28}$$

with the condition that $\alpha_\eta < (2)^{\frac{1}{2}}$. This upper limit for α_η is approached by the highest molecular weight sample (S1159) studied in toluene; in this case, the coefficient of z in equation (27) is 1·44. Thus, it is clear why equations (17) and (24) are so close numerically; such agreement between these two approaches to the problem of the excluded volume is assuring.

A_2–$[\eta]$–M *relationships*

In this section, the second virial coefficient data are analysed with respect to several relationships involving both the molecular weight and the intrinsic viscosity in a good and poor solvent. First, the observed molecular weight dependence of A_2' (in cyclohexane) will be compared with that predicted by several two-parameter theories. All data are then considered with respect to the empirical $\log A_2/\log M$ relationship. Next, Krigbaum's method[53] of obtaining the unperturbed dimensions of polymers is analysed and compared with other methods just described. Finally, the data are examined in view of recent findings on polystyrene solutions in decalin and toluene.

Comparison with theoretical $A_2\,(M)$ *relationships*

Theoretical expressions for the molecular weight dependence of A_2 are sometimes generalized by

$$A_2 = Y\, F(X) \tag{29}$$

where Y is a constant factor for a given polymer–solvent system, and $F(X)$ is some decreasing function of M. (The notation adopted here is identical to that used by Fox *et al.*[55].) Various treatments lead to different $F(X)$ functions, three of which will be considered in detail.

The constant Y is given by

$$Y = (\bar{v}^2/V_1)\, \psi_1\, (1 - \theta/T) \tag{30}$$

and is related to the polymer–solvent parameter B [see equation (23)]. For the polystyrene–cyclohexane system at 50°C, one calculates a value of $Y = 14{\cdot}5 \times 10^{-5}$, using $\psi_1 = 0{\cdot}38$; this relatively recent value for ψ_1 was reported in a very careful study by Orofino and Mickey[3]. It should be mentioned that this direct calculation of Y differs from that used by Fox and co-workers[55]. As noted previously, several widely different values of the entropy parameter have been reported; the reason for this selection of $\psi_1 = 0{\cdot}38$ will be considered later.

Different approximate treatments for the dependence of A_2 on M have been proposed by Flory, Krigbaum and Orofino[56, 57] (FKO), Casassa and Markovitz[58] (CM–I), and Casassa[59] (CM–II); other expressions[60-63] for $A_2\,(M)$ have been briefly discussed by Cassasa and Stockmayer[64]. The FKO and CM–I theories predict

$$F(X)_{FKO} = (4/\pi^{\frac{1}{2}} X)\, \ln\,(1 + \pi^{\frac{1}{2}} X/4) \tag{31}$$

and

$$F(X)_{CM\text{-}I} = (1 - e^{-1\cdot093X})/1\cdot093\,X \tag{32}$$

where

$$X = 4C_m\psi_1(1 - \theta/T)\,M^{\frac{1}{2}}/\alpha^3 \tag{33}$$

and

$$C_m = 1\cdot42 \times 10^{-24}\,(\bar{v}^2/V_1)\,(\Phi/K) \tag{34}$$

The CM–II theory, however, defines X by

$$X = 1\cdot507\,(\alpha_2^2 - 1) \tag{35}$$

with

$$\alpha_2^5 - \alpha_2^3 = 1\cdot601\,(\alpha^5 - \alpha^3) \tag{36}$$

and $F(X)$ is still given by equation (32).

Assuming $K_\theta = 8\cdot2 \times 10^{-4}$, the expansion factors, α, for each sample were derived from equation (21) and the relationship between α_η and α

$$\alpha_\eta^3 = \alpha^{5/2} \tag{37}$$

proposed by Yamakawa and Kurata[65, 66]. It may be mentioned here that this distinction between α and α_η has been applied throughout, although this difference for the polystyrene–cyclohexane system at 50°C is negligible.

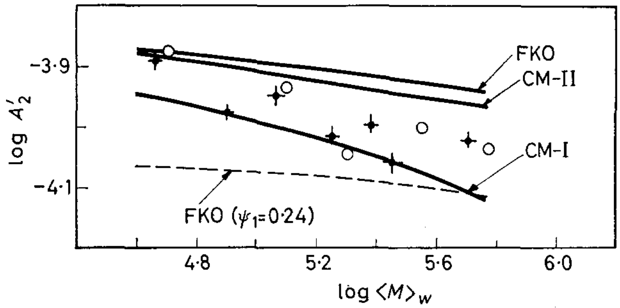

Figure 8—Molecular weight dependence of the second virial coefficient of polystyrene in cyclohexane at 50°C. Crosses, light scattering; circles, Krigbaum's osmometry data[22]

Figure 8 illustrates the molecular weight dependence of A_2' as predicted by theory for the polystyrene–cyclohexane system at 50°C*. The relative magnitude of these curves is similar to those calculated in two different studies of dilute solutions of polymethyl methacrylate[55, 64]. The light scattering data are indicated by crosses, while Krigbaum's earlier osmometry data[22] on carefully fractionated samples are represented by circles. Although the expected decrease in A_2' (or A_2) with M is apparent in these data, the results are too scattered to provide definite support for any of these theories. The fact that these data compare fairly well in regard to the *magnitude* of A_2 suggests that the selected value of $\psi_1 = 0\cdot38$ may be reasonably close to the true value. This point will be elaborated further in the discussion.

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*A value of $\Phi_0 = 2\cdot5 \times 10^{21}$ was assumed in these calculations; use of a lower value of $2\cdot2 \times 10^{21}$ does not significantly alter the calculated values of A_2.

The empirical log $A_2/\log M$ *relationship*

The observed decrease in A_2 with increasing molecular weight is sometimes conveniently expressed as a linear relationship between $\log A_2$ and $\log M$, i.e. $A_2 \sim M^{-\gamma}$. In their review of the dilute solution properties of flexible polymers, Kurata and Stockmayer[42] conclude that the largest possible value of γ should be $\sim 0{\cdot}10$ in a limited range of M, although much higher values have sometimes been reported. These higher values have been attributed to either spurious data, the method of obtaining A_2 from osmometry data, or the use of 90° measurements for lower molecular weight samples by the light scattering method[42]. (In this study, all A_2' values were derived from Zimm plots.) Furthermore, values of $\gamma \sim 0{\cdot}10$ support the various two-parameter theories.

For the polystyrene–cyclohexane system at 50°C, the analysis of the light scattering data yields $A_2' \sim \langle M\rangle_w^{-0{\cdot}13}$, while in the thermodynamically good solvent (toluene at 30°C), one obtains $A_2 \sim \langle M\rangle_w^{-0{\cdot}13}$. (If one excludes data obtained on the two lowest molecular weight samples, one finds $A_2 \sim \langle M\rangle_w^{-0{\cdot}07}$.) It is apparent that the molecular weight dependence of A_2, as expressed by this simple relationship, is not unusually large.

It is well known that the value of A_2 derived from osmotic pressure data is influenced by the treatment of data, due to the effect of the third virial coefficient, A_3. (All data reported here were analysed from plots of $(\pi/c)^{\frac{1}{2}}$ against c at four or more concentrations.) Furthermore, it has been shown[42] that the resulting molecular weight dependence of A_2 (i.e. the value of γ) is also quite different.

To examine this point a bit further, light scattering measurements were performed on two samples in toluene at 50°C, the same conditions employed in the osmometry determinations. These Zimm plots exhibited some curvature, in contrast to the linear plots obtained in the poor solvent cyclohexane; for this reason A_2' values were derived from a least squares analysis of $(Kc/R_{\theta=0})^{\frac{1}{2}}$ versus c, similar to the treatment of osmotic pressure data. For sample S108, one finds $A_2' = 4{\cdot}2_4 \times 10^{-4}$ in comparison with $A_2 = 4{\cdot}5_6 \times 10^{-4}$ by osmometry. Likewise, one obtains $A_2' = 4{\cdot}5_6 \times 10^{-4}$ with sample NBS705 while from osmotic pressure measurements, $A_2 = 4{\cdot}7_5 \times 10^{-4}$. (The weight-average molecular weights of each sample were identical with those determined in cyclohexane.) Also, one notes that Berry's data[67] on sample S108 in toluene at 12°C give $A_2 = 4{\cdot}0 \times 10^{-4}$, in close agreement with these results. The temperature difference between these measurements is negligible due to the fact that $[\eta]$ does not vary with temperature for polystyrene in toluene. These data lend support to square-root method of treating osmotic pressure data.

Krigbaum's semi-empirical equation

It is instructive to examine these data with respect to the semi-empirical relationship proposed[53] and later tested[68] by Krigbaum, namely

$$[\eta] = [\eta]_\theta + 4{\cdot}6 \times 10^{-3} A_2 M \qquad (38)$$

where $[\eta]_\theta$ is given by equation (11) and it is assumed that $\Phi = 2{\cdot}2 \times 10^{21}$. For heterogeneous polymers, the weight-average molecular weight should be used here, as Krigbaum has shown. This equation is very similar to the Stockmayer–Fixman relationship [cf. equation (25)]. Hence, a plot of $[\eta]/M^{\frac{1}{2}}$ against $M^{\frac{1}{2}}$ should yield K_θ. Since the thermodynamic quantity B is assumed to be independent of M, it is evident that the major difference between equations (38) and (25) is the slight molecular weight dependence inherent in A_2.

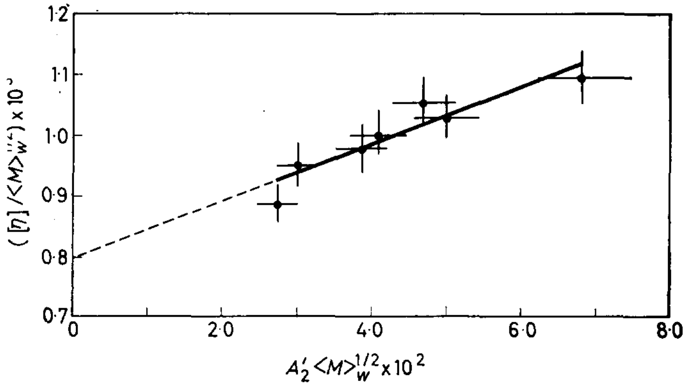

Figure 9—Krigbaum viscosity plot for polystyrene–cyclohexane system at 50°C

This analogy with the Stockmayer–Fixman relation is illustrated in *Figure 9* for the polystyrene–cyclohexane system. A linear regression yields $K_\theta = 7{\cdot}9_7 \times 10^{-4}$ and a slope of $4{\cdot}6_9 \times 10^{-3}$, in good agreement with prediction. This value of K_θ agrees well with that found earlier. Unfortunately,

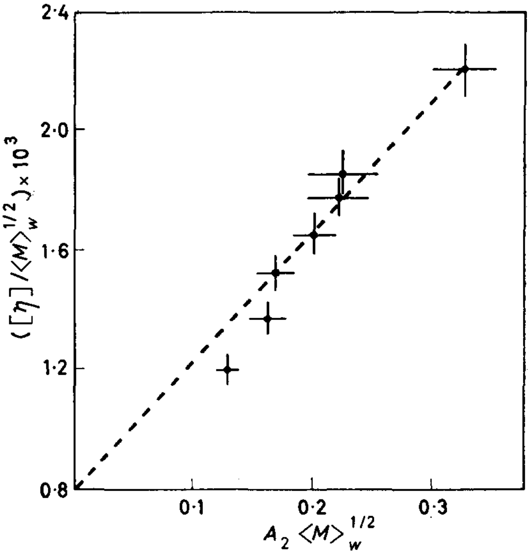

Figure 10—Krigbaum viscosity plot for polystyrene–toluene system at 25°C

the scatter in A_2 obtained by osmometry does not yield as good a correlation. However, if one arbitrarily selects data for the five highest molecular weight samples, one obtains an intercept and slope of $7{\cdot}8_2 \times 10^{-4}$ and $4{\cdot}3 \times 10^{-3}$ respectively, as shown by the dashed line in *Figure 10.* For these data, it seems that the A_2 values for samples S102 and C3 in toluene are greater than expected.

Analysis of these data by means of both the Krigbaum and Stockmayer–Fixman equations has demonstrated the fact that the slight molecular weight dependence of A_2 does not drastically affect the derived value of K_θ. However, as pointed out by Stockmayer and Fixman, the experimental difficulty of obtaining accurate A_2 values advocates the use of equation (25), as shown by data on the polystyrene–toluene system. Nevertheless, such analyses may easily be made since A_2 and M are derived simultaneously.

Other correlations with A_2, M and $[\eta]$

Another common method of data analysis is to consider the dimensionless ratio $A_2M/[\eta]$ as some function of the expansion factor α (or α_η). Stockmayer's review[69] suggests a few such correlations of which only three will be considered here. Hopefully, plots of $A_2M/[\eta]$ against (α^2-1) should describe a single 'master curve' for all narrow-distribution polymers in any solvent. The present data obtained in both good and poor solvents provide a means of testing this goal, since the value of K_θ [and thus α through equations (21) and (37)] is known. Frequently, the latter uncertainty as well as the usual difficulty in obtaining accurate A_2 data probably has made such analyses difficult, particularly with unfractionated samples.

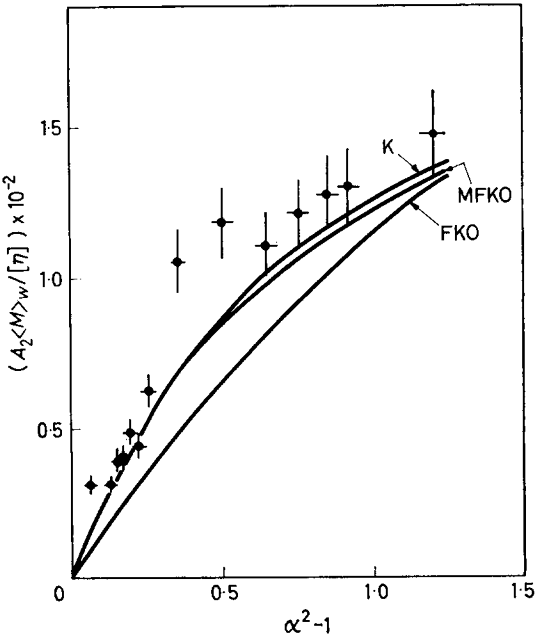

Figure 11—Plot of $A_2M/[\eta]$ against (α^2-1) for both solvent systems

It can be shown that the Flory–Krigbaum–Orofino (FKO) expression [equations (29), (30) and (31)] becomes

$$A_2M/[\eta]=414\log[1+0{\cdot}886(\alpha^2-1)] \tag{39}$$

assuming $\Phi=2{\cdot}2\times10^{21}$. This equation has often been used to calculate the expansion factor from determinations of A_2, M and $[\eta]$ when K_θ is unknown. By adjusting constants to force agreement with perturbation theories at low z, Stockmayer[69] has also proposed a modification of equation (39) to obtain

$$A_2M/[\eta]=165\log[1+4{\cdot}50(\alpha^2-1)] \tag{40}$$

Also, it can be shown that Krigbaum's expression [equation (38)] can be arranged to yield

$$A_2M/[\eta]=217(1-\alpha_\eta^{-3}) \tag{41}$$

again using $\Phi=2{\cdot}2\times10^{21}$. (For the wide range of α considered here, there may be some objection to the assumption of a constant value of Φ in these equations. For example, Krigbaum and Carpenter[70] have shown that Φ decreases by about 25 per cent with increasing solvent power; this change is of course appreciable and deserves further study.)

These predicted variations of $A_2\langle M\rangle_w/[\eta]$ with (α^2-1) are shown in *Figure 11*, where 'MFKO' designates the modified Flory–Krigbaum–Orofino expression [equation (40)]. The experimental data are represented by crosses for both cyclohexane and toluene. It is apparent that the Krigbaum equation more closely approximates the observed change in $A_2\langle M\rangle_w/[\eta]$ with (α^2-1). (As noted before, the A_2 values for the two lowest molecular weight samples, measured in toluene, again appear to be a bit high.) These data suggest that Krigbaum's relationship provides a better means of estimating α from A_2, M and $[\eta]$ data when the value of K_θ is unknown. Furthermore, it is seen that the original FKO equation overestimates the expansion factor, α.

Berry[67, 71, 72] has recently completed an extensive study of narrow-distribution polystyrene in decalin and toluene over a wide range of temperatures. These results are in excellent support of various two-parameter theories of dilute polymer solutions. Using his notation,

$$A_2=4\pi^{3/2}N_AB_BF'(z) \tag{42}$$

where $F'(z)$ represents some molecular-weight dependent factor,

$$z=[\langle S^2\rangle_0/M]^{-3/2}B_BM^{\frac{1}{2}} \tag{43}$$

and

$$\alpha^2=1+(134/105)z+\ldots\ldots \tag{44}$$

from various formulations of the excluded volume effect. Upon ignoring the $F'(z)$ factor, these equations yield

$$A_2M^{\frac{1}{2}}=[4N_A\pi^{3/2}(\langle S^2\rangle_0/M)^{3/2}/(134/105)](\alpha^2-1)+\ldots\ldots \tag{45}$$

Thus, equation (45) predicts linear plots of $A_2M^{\frac{1}{2}}$ against (α^2-1) and should provide a simple means for estimating $\langle S^2\rangle_0/M$ from data obtained in either good or poor solvents. It is interesting that Krigbaum's equation and equation (45) are similar, but the application of the latter assumes knowledge of K_θ.

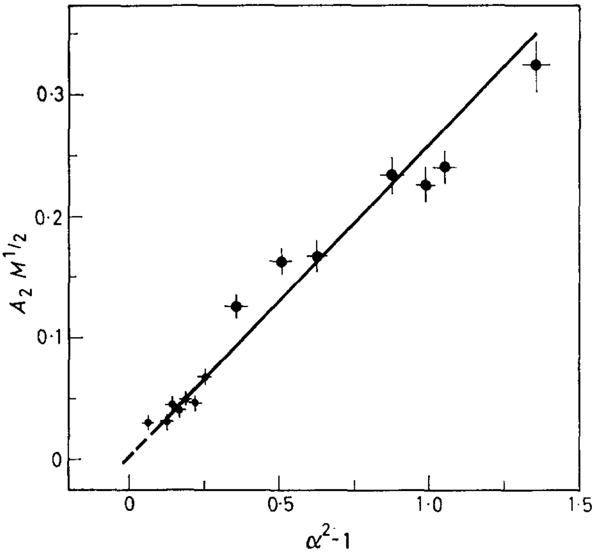

Figure 12—Plot of A_2M against (α^2-1) for both solvent systems

Figure 12 illustrates such linearity for both the light scattering and osmometry data assuming $K_\theta = 8{\cdot}2 \times 10^{-4}$. A linear regression of all the data yields $2{\cdot}6 \times 10^{-3}$ for the intercept at $\alpha = 1$ and the slope gives $10^{18}\langle S^2\rangle_0/M = 8{\cdot}6_3$, in fair agreement with Berry's value of 7·5. If one also assumes a value of 10^{-21} $\Phi_0 = 2{\cdot}5$, the calculated value for this characteristic ratio $10^{18}\langle S^2\rangle_0/M$ is 7·9 [from equation (9) under theta conditions]. Consequently, as Berry points out, equation (45) is a good approximation for data extending over a wide range in α; however, its direct application requires an *a priori* value for K_θ.

DISCUSSION

Since the completion of this study, a number of publications have appeared on the various methods for determining the unperturbed dimensions of polymers from $[\eta]/M$ data. In addition to the methods considered earlier, several other modifications and relationships have been proposed[73-75]. In a critical analysis of all these methods, Cowie[75] has shown that their utility depends somewhat upon the range of α (or M) and, in the range of molecular weight considered here, the most useful approach is that due to the Stockmayer–Fixman equation. These data are also in agreement with this conclusion.

The preceding analysis of $A_2(M)$ data with three approximate theories has shown that the slight decrease in A_2 with increasing M is predicted in all cases, but the scatter in these data precludes support for a specific theory. Nevertheless, the magnitude of A_2 calculated for this comparison is seen to be approximately correct provided a careful choice of the entropy parameter, ψ_1, is made. This selection of ψ_1 for the polystyrene–cyclohexane system deserves further comment at this time.

As mentioned earlier, an examination of the literature reveals several widely different values of ψ_1 for this system, depending somewhat upon the method for estimating this very important parameter. For the comparison of the present data with various theories in *Figure 8*, it was mentioned that the second virial coefficients were calculated using $\psi_1 = 0{\cdot}38$. If one calculates $A_2(M)$ using $\psi_1 = 0{\cdot}24$, these would predict $A_2(M)$ *lower* than any of the experimental data (indicated by the dashed curve in *Figure 8* for the FKO theory). Therefore, if one assumes that these theoretical treatments predict the correct *magnitude* of A_2, then one may conclude that $\psi_1 \simeq 0{\cdot}38$ is close to the true value for the polystyrene–cyclohexane system.

It was also shown that three different methods for analysing intrinsic viscosity–molecular weight data provide a means of estimating the viscosity constant, K_θ, if the viscosity measurements were performed in a 'poor' solvent for the polymer. From equations (14), (22) and (25), it is apparent that such methods are also expected to give estimates of B (or ψ_1). The present data yield ψ_1 values of 0·14, 0·24 and 0·22 for the FFS, SF and KSR methods respectively. (Upon using Stockmayer's modification[40] of Flory's constant C_m, the first of these values, $\psi_1 = 0{\cdot}14$, would change to 0·28.) Thus, the value of ψ_1, obtained through the use of the SF equation, when compared to $\psi_1 \simeq 0{\cdot}38$ is only about 60 per cent of this value.

Similarly, for the polystyrene–toluene system, one can derive a value of B from the corresponding plots of the KS and SF methods. In this case, such a comparison yields B values which are only about 30 per cent of the recent estimate made by Berry[67] for this system.

It therefore appears that the KS and SF methods may give B (or ψ_1) values which are too low, while K_θ can be estimated quite well within this limited (but practical) range of molecular weight.

It has also been demonstrated that in both good and poor solvents, these polystyrene data can be fitted fairly well by Krigbaum's semi-empirical equation. In addition, in generalized plots of $A_2M/[\eta]$, this relationship again provides the best agreement with the experimental results. Also noteworthy is the fact that the FKO equation predicts a greater expansion factor than observed, over the whole range of α considered. Similarly, a linear relation exists between $A_2M^{\frac{1}{2}}$ and $(\alpha^2 - 1)$ for both solvent systems, as Berry has shown over a comparable range in α.

The writer is pleased to acknowledge the assistance of Messrs F. G. Haliczky and J. A. Kocsis for their careful experimental work. He is indebted to the late Dr H. C. McCormick (The Dow Chemical Company) and to Dr C. E. Geacintov for supplying the polystyrene samples. He also thanks the Mobil Chemical Company for its encouragement and support of this investigation.

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(*Received July 1968*)

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