tant to attach much significance to these differences at the present time.

Figure 11 is an attempt at a similar correlation for the compliances. Values of J_R were calculated with eq 4 for each solution. The parameter $\bar{M}_z\bar{M}_{z+1}/\bar{M}_w^2$ was taken to be 1.26 for the fractions, corresponding to a Zimm-Schulz distribution with Z = 10, and 3.0 for the whole polymers, the value appropriate for the most probable distribution (Z = 0). As with τ_R/τ_0, the values of J_R/J_e for the polydisperse samples do not follow quite the same locus as the fractions when $cM_w/\rho M_c$ is the correlating variable. With $c\bar{M}_n/\rho M_c$, however, the relative positions of the polydisperse samples is shifted to the left and the agreement between the two distribution types is improved. Again, there are not enough samples involved to justify a choice. The major point is the agreement between data on poly(vinyl acetate) and polystyrene, which is as good as in the τ_R/τ_0 correlation.

The possible generality of the τ_R/τ_0 *vs.* $cM/\rho M_c$ correlation for all linear polymers in the entanglement region was suggested earlier.[19] Viscosity–shear rate behavior for fractions of polydimethylsiloxane[20] (M_c = 24,500[16]) and linear polyethylene[21] (M_c = 3,800[16]) have recently been published, and earlier results on narrow-distribution polybutadiene[22] (M_c = 5900[16]) are also available. The polydimethylsiloxane values agree nicely with those in Figure 10, but, as they only extend to M/M_c values of 4, agreement in the slope of the line is difficult to judge. The values of τ_R/τ_0 for polyethylene extend to very high values of M/M_c, but all appear to lie well below the line in Figure 10. The polybutadiene data, on the other hand, lie somewhat above the line; an M_c value of approximately 10,000 instead of 5900 would be needed to produce agreement with the polystyrene and poly(vinyl acetate) results. The validity of these comparisons depends of course on the absolute accuracy of viscosity measurements among different investigators as well as the absence of branching and the narrowness of the fractions used in each case. More data on other polymers and comparisons of measurements among investigators are needed before the factors that control τ_R/τ_0 in general can be defined.

Compliance data have been published for narrow-distribution samples of poly(α-methylstyrene)[23] (M_c = 28,000) and poly(methyl methacrylate)[24] (M_c variable and dependent on temperature and tacticity[16]). For poly(α-methylstyrene) J_R/J_e *vs.* M/M_c is approximately linear, but with a lower slope than Figure 11; a value of $M_c \approx 20{,}000$ would produce agreement. The compliances for poly(methyl methacrylate) appear to be very near J_R even well into the entanglement region. Some earlier measurements on undiluted poly(vinyl acetate) fractions[17] also show little if any systematic departure from values of J_R. The generality of the J_R/J_e *vs.* $cM/\rho M_c$ correlation is thus also somewhat uncertain, and again measurements on other narrow-distribution polymers and comparisons among investigators are needed.

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Gel Permeation Chromatograph Calibration. Intrinsic Viscosity–Polydispersity Effect

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ABSTRACT: A quantitative discussion of the dependence of the intrinsic viscosity on the polydispersity of a polymer is given. The polydispersity–viscosity parameter (δ) is introduced to compensate for the effect of polydispersity on the measured intrinsic viscosity. The magnitude of the polydispersity effect is shown by assuming a log normal distribution as the distribution function of a polymer. A simple computer approach for calibrating a gel permeation chromatograph with several BMWD linear polymers is presented. Generation of the universal gel permeation chromatograph calibration of Benoit from both narrow and broad molecular weight distribution standards is used to demonstrate that the universal calibration is universal only if the polydispersities of the standards used are taken into account.

The advent of gel permeation chromatography has provided the technique for the rapid molecular weight[1] characterization of polymers. To utilize the technique, the gel permeation chromatograph must be calibrated for the particular polymer type of interest, *i.e.*, the molecular weight of polymer molecules as a function of their elution volumes from the gel permeation chromatography column must be determined.

The accepted method of calibrating a gel permeation chromatograph is to use narrow molecular weight distribution standards of the same polymer type which is to be investigated to obtain the elution volume–molecular weight relationship. This is not always possible, since narrow molecular weight distribution (NMWD) standards of the polymer type of interest may not be available. To circumvent the lack of NMWD standards, techniques which allow the gel permeation chromatograph to be calibrated with broad molecular weight distribution (BMWD) standards or theoretical ap-

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proaches which allow calibration for one polymer type by another polymer type are required.

Hamielec, *et al.*,[2] have suggested a technique for calibration with one or two BMWD standards employing a Rosenbrock search procedure. In this paper a simpler computer approach is presented which uses one, two, or more BMWD standards of known weight and number-average molecular weights to obtain the calibration.

Benoit, *et al.*,[3] have suggested the "universal GPC calibration" which should be applicable to all polymers. This approach utilizes the concept that the polymer molecules are separated in the gel permeation chromatography process by their differences in hydrodynamic volume. The hydrodynamic volume, molecular size in solution, is proportional to the product of the intrinsic viscosity and the molecular weight of the polymer molecule. The intrinsic viscosity and either the weight- or number-average molecular weight of NMWD standards have been used to obtain this product as a function of the elution volume of the standards. However, in the application of this concept it is necessary to compensate for the effect of polydispersity on the measured intrinsic viscosity of the standards used. A quantitative discussion of the dependence of the intrinsic viscosity on the polydispersity of a polymer is presented. In addition, it is demonstrated that the universal gel permeation chromatograph calibration is truly universal only if the polydispersities of the standards used are taken into account. This demonstration is accomplished by generating the universal gel permeation chromatograph calibration from NMWD ($\bar{M}_w/\bar{M}_n < 1.21$) standards of linear polystyrene and BMWD ($\bar{M}_w/\bar{M}_n > 3.0$) standards of linear polyethylene.

Experimental Section

A Water's Associates Model 100 gel permeation chromatograph equipped with the R4 refractometer modification was used for these experiments. The columns used were four 4-ft Water's Associates Styragel columns: 2×10^4, 10^5, 3×10^6, and 10^7 Å. The gel permeation chromatography solvent used was redistilled trichlorobenzene containing as antioxidant 0.7 g/l. of 2,6-*tert*-butyl-*p*-cresol. The system was operated at 130°. All polymer solutions injected were approximately 0.3 wt %.

The two sets of standards used were (1) NMWD linear polystyrenes ($\bar{M}_w/\bar{M}_n < 1.21$) commercially available from Water's Associates and (2) BMWD linear polyethylenes ($\bar{M}_w/\bar{M}_n > 3.0$) from E. I. du Pont de Nemours and Co., Inc.

The intrinsic viscosity measurements were obtained with a Hewlett-Packard autoviscometer using Ubbelohde viscometers (ASTM D 445) in the gel permeation chromatography solvent at the gel permeaiton chromatography tempeiature (trichlorobenzene, 130°). Solution concentrations are expressed in units of weight per cent.

The data collected in these experiments were processed with the aid of an IBM 1130 computer.

Results and Discussion

A. Intrinsic Viscosity–Polydispersity Effect. To determine the effect of polydispersity ($\bar{M}_w/\bar{M}_n$) on the intrinsic viscosity ($[\eta]$) of a polymer sample, consider the empirical Mark–Houwink expression

$$[\eta] = KM^a \text{ or } [\eta] = K\bar{M}_v^{\,a} \qquad (1)$$

For polydispersed polymers, it is generally assumed that the same expression holds if the weight-average molecular weight ($\bar{M}_w$) is used.

$$[\eta] = K\bar{M}_w^{\,a} \qquad (2)$$

However, when measurements made on polydispersed polymers are fitted to eq 2, the values calculated for K and a are not the correct values for monodispersed polymers. Furthermore, when polymers of different degrees of polydispersity are compared, anomalies can result. In short, if eq 2 is applied to polydispersed systems, then the apparent values of K and a will change with the degree of polydispersity. This is not the most convenient way to treat polydispersed polymers. A more convenient alternative is to fix K and a at the correct level for monodispersed polymers and express the intrinsic viscosity–weight-average molecular weight relationship as follows

$$[\eta] = K\bar{M}_w^{\,a}(1 - \delta) \qquad (3)$$

where δ is a function of the polydispersity.

To calculate the value of the polydispersity–viscosity parameter δ, the shape of the molecular weight distribution curve must be known or assumed. The log normal distribution function (eq 4)[4] is an adequate function to use since it describes a symmetrical gel permeation chromatogram (typical of NMWD polymers), but other functions could be employed.

$$W_m = (\sigma\sqrt{2\pi}\bar{M}_n)^{-1} \exp(-[\ln (M_m/\bar{M}_n) + \sigma^2/2]^2/2\sigma^2) \qquad (4)$$

where W_m = the weight fraction of component m, M_m = the molecular weight of component m, $\sigma = (\ln (\bar{M}_w/\bar{M}_n))^{1/2}$, and $\bar{M}_w = \bar{M}_n \exp(\sigma)^2$.

The intrinsic viscosity of a polymer sample can be calculated from eq 5 utilizing eq 4 provided the Mark–Houwink constants K and a of the monodispersed set of polymers are known

$$[\eta] = \sum_m [\eta]_m W_m = K\sum_m M_m^{\,a} W_m \qquad (5)$$

To determine the effect on δ of increasing the polydispersity of a polymer sample of any constant weight-average molecular weight, eq 3 and 5 were combined. The results show that δ is a function only of the Mark–Houwink exponent and the polydispersity; *i.e.*

$$\delta = 1 - \sum_m W_m M_m^{\,a}/[\sum_m W_m M_m]^a$$

In the limiting cases where $a = 1$ and when W_m is unity, δ is 0. Figure 1 is a plot of the polydispersity–viscosity parameter δ as a function of a and $\bar{M}_w/\bar{M}_n$ for a log normal distribution.

The effect of polydispersity on the intrinsic viscosity of a polymer sample as indicated in Figure 1 is far from negligible. For example, the difference in the intrinsic viscosity of two polymers of the same type and weight-average molecular weight with polydispersities of 1.1 and 5.0 is approximately 15% (assuming $a = 0.7$). For polymer samples with much smaller differences in polydispersity ($\bar{M}_w/\bar{M}_n$ of 1.10 and 1.35) the effect is still significant (approximately 2% with $a = 0.7$).

To determine the weight-average molecular weight of a polymer sample from the intrinsic viscosity measurement, the Mark–Houwink constants based on a monodispersed set and knowledge of the polydispersity of the sample (*i.e.*, δ) are required. In practice a knowledge of the polydispersity may not be available, but one should be cognizant of the error involved when polydispersity of the sample is not considered.

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B. Universal Gel Permeation Chromatograph Calibration. Moore's assumption[1] is used that the gel permeation chromatograph calibration for a monodispersed set of polymers is given by

$$\log M = A + BV_r \qquad (6)$$

over the desired molecular weight range, where V_r is the elution volume in milliliters of the mth component of molecular weight M and A and B are constants.

From eq 1 and 6, it follows that

$$\log (KM^{a+1}) = \log [\eta]M = A_v + B_vV_r \qquad (7)$$

where

$$A_v = A(a + 1) + \log K \qquad (8)$$

$$B_v = B(a + 1) \qquad (9)$$

and eq 7 is the form of the universal gel permeation chromatograph calibration.[3]

It is clear that if one has the normal gel permeation chromatograph calibration (eq 6) and the monodispersed Mark–Houwink constants (K and a) at the gel permeation chromatography conditions (solvent and temperature), then the coefficients of the universal gel permeation chromatograph calibration (A_v and B_v) are easily calculated. This is the procedure that was followed for both linear polyethylene and linear polystyrene utilizing the same set of columns. The normal gel permeation chromatograph calibration and monodispersed Mark–Houwink constants were obtained for linear polyethylene using BMWD standards and for linear polystyrene using NMWD standards, thus allowing the generation of the universal gel permeation chromatograph calibration from two independent sets of standards differing in both type and degree of polydispersity.

1. BMWD. Linear Polyethylene. The normal gel permeation chromatograph calibration for linear polyethylene was obtained by a computer procedure which adjusts the coefficients of eq 6 to fit the gel permeation chromatograph data (peak height *vs.* elution volume) to weight and number-average molecular weight data (by light scattering and osmometry, respectively) for several BMWD standards. The computer procedure requires an initial estimate of the slope (B) and intercept (A) of eq 6. The slope is determined first. The quantity $R(\bar{M}_w/\bar{M}_n)$ is calculated from the input weight and number-average molecular weights (*i.e.*, R_m) and from the input chromatogram and the estimates of the slope and intercept (*i.e.*, R_c) for each BMWD standard. The slope is then determined by varying the original estimate of the slope in a stepwise manner, holding the intercept constant, to minimize the differences between R_m and R_c for each standard simultaneously, *i.e.*, the expression

$$\sum_i[(R_c - R_m)/R_m]^2$$

is minimized. The intercept is then determined in an analogous manner by minimizing the differences between the measured and calculated weight-average molecular weights for each standard simultaneously, *i.e.*, the expression

$$\sum_i[((\bar{M}_w)_c - (\bar{M}_w)_m)/(M_w)_m]^2$$

is minimized.

The calibration obtained in applying this procedure to four BMWD linear polyethylene standards is given by

$$\log M = 11.9 - 0.0476V_r \qquad (10)$$

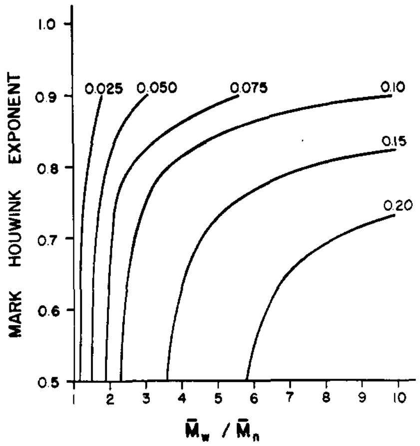

Figure 1. Polydispersity viscosity parameter, δ.

It should be noted at this point that "line broadening" of the chromatogram becomes increasingly important as the polydispersities of polymer samples decrease. The chromatograms of the narrower MWD polymers should be corrected for this effect, while for BMWD polymers the effect is minimized and correction may not be necessary. Several methods for correcting the chromatograms of the narrower MWD polymers for imperfect resolution have been reported[5–12] and will not be discussed here.

In obtaining the linear polyethylene calibration (eq 10), the effects of imperfect resolution in the chromatograms of the BMWD standards were automatically taken into account. The classical (light scattering and membrane osmometry) and gel permeation chromatography determined weight- and number-average molecular weights of the four BMWD linear polyethylene standards are given in Table I.

The variance between the classical and gel permeation chromatography determined weight- and number-average molecular weights is within the reliability of the classical values themselves, *i.e.*, approximately 10% variance.

The monodispersed Mark–Houwink constants for linear polyethylene were obtained by fitting the measured intrinsic viscosity to the molecular weight distribution of each BMWD standard simultaneously by eq 5. The molecular weight distributions were obtained from the normal gel permeation chromatograph calibration, eq 10, and the chromatograms

TABLE I

MOLECULAR WEIGHT OF LINEAR POLYETHYLENE

Standard	Classical $\bar{M}_w$	Classical $\bar{M}_n$	Gel permeation chromatography $\bar{M}_w$	Gel permeation chromatography $\bar{M}_n$
UC 1	62,800	19,900	64,200	20,100
UC 2	84,100	25,200	88,200	23,400
UC 3	112,000	18,800	110,000	17,600
UC 4	180,000	35,500	177,000	39,600

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Table II
Mark–Houwink Constants

Polymer	$K \times 10^4$	a
Linear polyethylene	4.95	0.715
Linear polystyrene	1.60	0.702

Table III
Intrinsic Viscosity. Linear Polyethylene

Sample	$[\eta]_m$[a]	$[\eta]_c$[a]
UC 1	1.19	1.20
UC 2	1.47	1.46
UC 3	1.60	1.58
UC 4	2.40	2.42

[a] Intrinsic viscosities are in units of reciprocal weight per cent.

Table IV
Universal Gel Permeation Chromatograph Calibration Coefficients

Polymer	A_v	B_v
Linear polyethylene	17.10	−0.0815
Linear polystyrene	16.80	−0.0798

Table V
Polydispersity–Viscosity Parameters

$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$[\eta]_m$[a]	δ
98,000	1.02	0.493	0.0020
173,000	1.05	0.767	0.0050
411,000	1.05	1.37	0.0050
867,000	1.12	2.25	0.0117
2,145,000	1.21	4.32	0.0197

[a] Intrinsic viscosities are in units of reciprocal weight per cent.

of each standard. The fit was accomplished by minimizing the expression

$$\sum_i [([\eta]_m - [\eta]_c)/[\eta]_m]^2$$

to obtain the constant K and exponent a, where $[\eta]_m$ is the measured intrinsic viscosity and $[\eta]_c$ is that calculated in the fit. The linear polyethylene Mark–Houwink constants determined by this procedure are given in Table II. The measured intrinsic viscosities and those calculated from the fit are given in Table III.

The universal gel permeation chromatograph calibration coefficients (A_v and B_v) are readily calculated from the Mark–Houwink constants, the coefficients of the normal gel permeation chromatograph calibration (eq 10), and eq 8 and 9. These coefficients are given in Table IV.

2. NMWD. Linear Polystyrene. The calibration for linear polystyrene was obtained by fitting elution volume–peak molecular weight data for several commercial NMWD standards. The gel permeation chromatograph calibration obtained is given by

$$\log M = 12.1 - 0.0469 V_r \tag{11}$$

The monodispersed Mark–Houwink constants for linear polystyrene were also obtained from the NMWD standards. The intrinsic viscosity and weight-average molecular weight data were fitted by eq 2 to obtain an estimate for the value of the Mark–Houwink exponent a. Knowing the polydispersity ($\bar{M}_w/\bar{M}_n$) of the standards and having an estimate of the exponent a, a value of the "polydispersity–viscosity parameter" is calculated by the procedure above for each NMWD standard and eq 3 is fitted to these data. Once the fit is obtained and a new value of the exponent a is determined, a new value of δ is calculated and eq 3 is refitted to these data, etc., until the value of a is constant. The monodispersed Mark–Houwink constants so calculated for linear polystyrene are given in Table II. The polydispersity–viscosity parameter calculated for each standard along with the weight-average molecular weight, polydispersity, and the measured intrinsic viscosity are given in Table V.

The universal gel permeation chromatograph calibration coefficients A_v and B_v can now be calculated from the linear polystyrene monodispersed Mark–Houwink constants, the coefficients of the normal gel permeation chromatograph calibration (eq 11), and eq 8 and 9. These coefficients are given in Table IV.

The variance in the coefficients calculated from the BMWD linear polyethylene and NMWD linear polystyrene standards is about 2%, which is within the reliability of the gel permeation chromatography instrument. The coefficients calculated by the two approaches can be considered equivalent.

The application of the universal gel permeation chromatograph calibration requires the knowledge of the monodispersed Mark–Houwink constants for the polymer type of interest. While these constants are readily attainable for most linear polymers, the application of this type of calibration to nonlinear or unknown polymers presents a problem. A technique is suggested to circumvent this problem.[13] The proposed technique involves the collection of a few fractions of the unknown polymer as it is being chromatographed. Data collected on known polymers on the same set of gel permeation chromatography columns would allow an estimate of the polydispersities of these fractions. With the estimate of the polydispersities and an intrinsic viscosity measurement on each fraction, a hypothetical intrinsic viscosity of a monodispersed polymer with elution volume equal to the elution volume of each fraction could be calculated. This would allow the expression of the "monodispersed" intrinsic viscosity as a function of the elution volume. This expression coupled with the universal gel permeation chromatograph calibration would provide the normal gel permeation chromatograph calibration (log M *vs.* V_r) for the unknown polymer.

Conclusions

The equivalency of the universal gel permeation chromatograph calibrations obtained from both broad and narrow molecular weight distribution polymer standards of different types when compensating for polydispersity indicates that this calibration is indeed universal. For this calibration, the intrinsic viscosity–molecular weight product used must be that of a monodispersed species, *i.e.*, the intrinsic viscosity must be expressed in terms of Mark–Houwink constants for a monodispersed set.

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(13) Private discussions with D. D. Bly and R. C. Williams of Du Pont.