Viscosity and Normal Stresses in Poly(vinyl acetate) Systems

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ABSTRACT: A series of linear poly(vinyl acetate) samples with known molecular weight distributions was prepared, characterized, and used as concentrated solutions in diethyl phthalate to study non-Newtonian viscosity and first normal stress difference in the entanglement region. Good agreement was found between the zero-shear viscosities and values reported by Nakayasu and Fox. The time constant governing shear-rate dependence of viscosity, τ_0, and steady-state shear compliance obtained from the normal stress behavior, J_e, were compared with τ_R and J_R, the characteristic time and compliance calculated for the Rouse model. The ratios τ_R/τ_0 and J_R/J_e were linear functions of the product cM. When compared as functions of the extent of penetration into the entanglement region, $cM/\rho M_c$, the ratios agreed quantitatively with data obtained earlier on polystyrene systems. The factors governing these correlations are still unclear and need further investigation in other polymer systems.

Recently an extensive study of non-Newtonian viscosity and normal stresses in polystyrene systems was reported,[1] involving samples of both narrow ($\bar{M}_w/\bar{M}_n \approx 1.1$) and moderately broad ($M_w/M_n \approx 2$) molecular weight distribution. Measurements were made on concentrated solutions (c = 0.20–0.55 g/ml) in *n*-butylbenzene, all solutions lying well within the entanglement region ($c\bar{M}_w > 35{,}000$ for polystyrene). Master curves were formed from the viscosity–shear rate data. The shapes of these curves appeared to be independent of c and $\bar{M}_w$ but were directly related to distribution breadth. Individual solutions were characterized by η_0, the viscosity at zero shear rate, τ_0, a time constant governing the shear-rate dependence in the viscosity, and J_e, the steady-state shear compliance, obtained from the first normal stress difference at low shear rates. Both τ_0 and J_e depended systematically on concentration and molecular weight according to the relations

$$\tau_0 = \frac{\alpha\tau_R}{1 + \beta c\bar{M}_w} \qquad (1)$$

$$J_e = \frac{\alpha' J_R}{1 + \beta' c\bar{M}_w} \qquad (2)$$

in which τ_R and J_R are the characteristic relaxation time and steady-state shear compliance of the Rouse model

$$\tau_R = (6/\pi^2)(\eta_0\bar{M}_w/cRT) \qquad (3)$$

$$J_R = (2/5)(\bar{M}_w/cRT)(\bar{M}_z\bar{M}_{z+1}/\bar{M}_w^2) \qquad (4)$$

The solvent viscosity η_s, always negligible compared to solution viscosity η_0, has been omitted from the expression for τ_R in eq 3.

The forms of eq 1 and 2 were most clearly evident in the data on narrow distribution samples. Measurements of τ_0 and J_e on undiluted polystyrenes of narrow distribution[2–4] conform to the same equations (with c replaced by polymer density ρ) with virtually the same values of the constants α, α', β, and β'. Since the data on undiluted samples were collected in the temperature range 160–200°, the constants appear to be practically independent of temperature and unaffected by the presence or absence of solvent. The present investigation seeks to test eq 1 and 2 on another polymer system, and particularly to determine how much the constants change when a different polymer is used. A second purpose is to provide data for clarifying the effects of branching on rheological properties. In a recent study of branched poly(vinyl acetate)[5] the viscosity master curves were found to be insensitive to the distribution broadening caused by branching reactions, and τ_0 and J_e were essentially proportional to τ_R and J_e without a residual $c\bar{M}_w$ dependence. Measurements on linear poly(vinyl acetate) are needed to separate branching effects from those due only to molecular weight distribution.

Sample Preparation and Characterization

Two groups of poly(vinyl acetate) samples were prepared, one for fractionation to provide narrow-distribution samples, the other for use directly as samples with most probable molecular weight distribution. All polymerizations were conducted at low conversion to avoid branching. Vinyl acetate (Union Carbide, 99+% purity) was distilled under partial vacuum into ampoules containing the free-radical initiator azobisisobutyronitrile. Initiator concentration was approximately 4×10^{-5} M in all cases. After degassing, the ampoules were sealed under vacuum and placed in a constant-temperature bath at 60°. The reaction was stopped after approximately 3.5 hr to obtain conversions of 3–4%, the ampoules were opened, and the polymer was isolated by precipitation with hexane. A total of 300 g of poly(vinyl acetate) was accumulated for fractionation in this manner.

The same procedures were used to prepare six samples for use as polydisperse specimens, except that ethyl acetate (CP grade) was added in different proportions to each as a transfer agent. Polymerization times ranged from 6 to 18 hr; conversions of monomer to polymer were between 5.6 and 10%. Theory and previous experience[6,7] indicate essentially linear polymers under these conditions, each sample having very nearly an exponential distribution of molecular weights.

Fractionation was accomplished by selective extraction with solvent–nonsolvent mixtures. The polymer was deposited on stainless-steel mesh, solutions of methyl ethyl ketone and *n*-hexane were passed over the mesh, and the extracted polymer was recovered by precipitation with water. Details of the apparatus and procedure are available[8] and will be pub-

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(1) W. W. Graessley and L. Segal, *Macromolecules*, 2, 49 (1969).
(2) R. A. Stratton, *J. Colloid Interface Sci.*, 22, 517 (1966).
(3) W. M. Prest, Jr., *J. Polym. Sci., Part A-2*, 8, 1897 (1970).
(4) D. J. Plazek and V. M. O'Rourke, *ibid., Part A-2*, 9, 209 (1971).
(5) W. W. Graessley and J. S. Prentice, *ibid., Part A-2*, 6, 1887 (1968).
(6) W. W. Graessley, R. D. Hartung, and W. C. Uy, *ibid., Part A-2*, 7, 1919 (1969).
(7) K. Nagasubramanian and W. W. Graessley, *Chem. Eng. Sci.*, 25, 1559 (1970).
(8) W. C. Uy, Ph.D. Dissertation, Northwestern University, 1969.

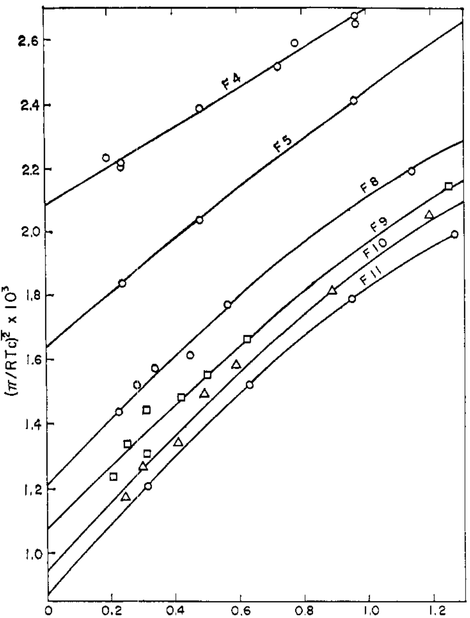

Figure 1. Osmotic pressure *vs.* concentration in toluene for high molecular weight fractions of poly(vinyl acetate).

lished elsewhere. A total of 26 fractions was collected. Ten were selected for characterization and five were ultimately used in the rheological studies.

Intrinsic viscosities were measured in methyl ethyl ketone at 34.7°. Weight-average molecular weights were determined by light scattering at 35° in a Brice-Phoenix light scattering photometer (Model 2000) with methyl ethyl ketone as the solvent. Number-average molecular weights were determined by osmometry at 34.1° in a Dohrmann-Shell automatic membrane osmometer with toluene as the solvent. Extreme care was required in the latter experiments because of the high molecular weights involved. Figure 1 shows the osmometry data and the extrapolation to obtain $(\pi/c)_0$ for the fractions. The uncertainty in $\overline{M}_n$ is believed to be no worse than 15% in the highest molecular weights and correspondingly better at lower molecular weights. The details of procedure and calibration in all the above measurements are given elsewhere.[6,8]

Distributions were also examined on a gel permeation chromatograph (Water Associates) at 30° with tetrahydrofuran as solvent. The chromatographs were not corrected for axial dispersion. Uncorrected $\overline{M}_w/\overline{M}_n$ ratios ranged from 1.19 to 1.24 for the fractions, values no larger than those obtained in the same instrument for the standard calibration polystyrenes (measured $\overline{M}_w/\overline{M}_n$ ratios in the range 1.01–1.15).

All characterization data are shown in Table I. In general the fractions, except for F4, appear to have $\overline{M}_w/\overline{M}_n$ ratios less than 1.15. The unfractionated samples have $\overline{M}_w/\overline{M}_n$ ratios near 2.0, the theoretical value for most probable distributions. The viscosity-average molecular weight $\overline{M}_v$ was calculated from $\overline{M}_w$ for the unfractionated samples on the assumption of a most probable distribution: $\overline{M}_v/\overline{M}_w = [(1 + a)\Gamma(1 + a)]^{1/a}/2 = 0.935$ for $a = 0.71$, the viscosity exponent in poly(vinyl acetate)–methyl ethyl ketone systems.[9] For the fractions, $\overline{M}_v$ was taken to be equal to $\overline{M}_w$. Figure 2 shows the correlation of $[\eta]$ with $\overline{M}_v$. Values obtained for linear polymers in earlier studies[6,7] are also included for comparison. The dotted line is the correlation reported for linear poly(vinyl acetate) in methyl ethyl ketone by Ohyanagi and Matsumoto.[9] There seems to be no evidence of branching, which would be indicated by low values of $[\eta]$, even in the highest molecular weight fractions.

TABLE I
CHARACTERIZATION DATA FOR EXPERIMENTAL SAMPLES

Sample no.	$[\eta]$	$\overline{M}_n/10^5$	$\overline{M}_w/10^5$	$\overline{M}_w/\overline{M}_n$	$(\overline{M}_w/\overline{M}_n)_{GPC}$
F4	0.904	2.31	2.98	1.29	1.24
F5	1.09	3.72	3.97	1.07	1.24
F8	1.70	6.83	7.88	1.15	1.24
F9	2.14	8.66	9.30	1.07	1.22
F10	2.35	11.2	12.2	1.08	1.22
F11	2.81	13.2	13.9	1.05	1.22
B1	0.947	1.81	3.17	1.75	2.26
B3	1.26	2.45	5.08	2.07	2.53
B4	1.42	2.58	5.56	2.15	2.49
B6	1.67	3.76	7.25	1.93	2.55

Rheological Measurements

The polymers were freeze dried from benzene, weighed, and then combined with known volumes of diethyl phthalate (CP grade). Concentrations were calculated from the densities, 1.19 for poly(vinyl acetate) and 1.12 for diethyl phthalate, assuming additivity of volumes. The mixtures were dissolved by heating in stoppered bottles at 40° for approximately 1 month. Concentrations ranged from 0.171 to 0.349 g/ml. The value of M_c, the critical molecular weight in η_0 *vs.* M correlations, is 24,500 for undiluted poly(vinyl acetate).[10] The solutions represent $c\overline{M}_w$ products from 50,000 to 360,000, placing them all well within the entanglement region.

After the flow measurements the polymers were recovered by precipitation. Concentrations were checked by weighing the polymer reclaimed from aliquots of the solutions, and the absence of degradation was confirmed by intrinsic viscosity measurements on selected samples.

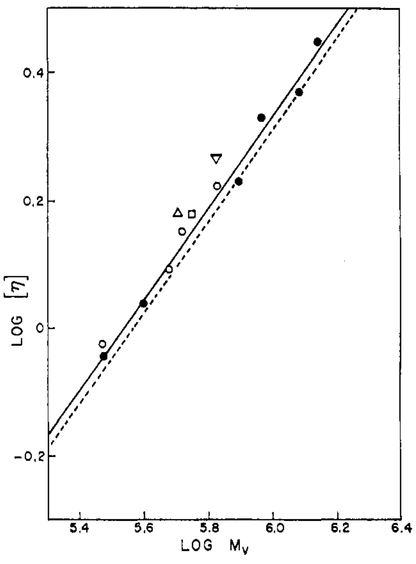

Figure 2. Correlation of intrinsic viscosity in methyl ethyl ketone with molecular weight for linear poly(vinyl acetate): ●, data on the fractions (F series); ○, data on the unfractionated samples (B series); remaining symbols, data obtained on linear unfractionated samples in other studies (see ref 6, 7); ---, the correlation of Matsumoto and Ohyanogi[9] for $[\eta]$ in methyl ethyl ketone; ——, a least-squares calculation for the current data only.

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(9) M. Matsumoto and Y. Ohyanagi, *J. Polym. Sci.*, **46**, 441 (1960).

(10) J. D. Ferry, "Viscoelastic Properties of Polymers," 2nd ed, Wiley, New York, N. Y., 1970.

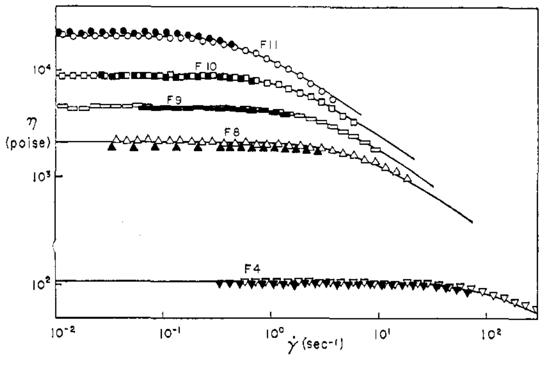

Figure 3. Viscosity *vs.* shear rate for several linear poly(vinyl acetate) fractions in diethyl phthalate solution (c = 0.171 g/ml): filled symbols, data collected with a 4° cone angle; open symbols, data collected with a 0.58° cone angle; ——, theoretical master curves[13] for $M_w/M_n = 1.09$ ($Z = 10$ in the Zimm-Schulz distribution).

Shear stress p_{12} and primary normal stress difference $p_{11} - p_{22}$ were determined as functions of steady shear rate $\dot\gamma$ with a plate–cone Weissenberg rheogoniometer (Model R-16). The plate diameter was 7.5 cm in all experiments; the cone angles were 0.583 and 4° for the shear-stress measurements and 4° only for the normal stresses. Experiments with the smaller cone angle were made with the normal-stress attachment removed because of the difficulty of achieving and maintaining a constant gap setting. While measuring normal stress (the 4° cone), it was found most convenient to bypass the servomotor in the normal-stress attachment and maintain the gap setting during operation by adjusting the normal-force micrometer manually. All measurements were made at 31.5°, this temperature being measured by a thermocouple imbedded in the platen and maintained by circulation of thermostated water through the platen enclosure.

Shear stress was calculated from the deflection of $^1/_8$- and $^1/_4$-in. torsion bars. The $^1/_{16}$-in. normal-stress spring was used in all normal-force measurements. The force–deflection behavior of this spring was found to be significantly nonlinear, making it necessary to convert each measured deflection to force with a calibration curve. Normal stress was calculated from the total flow-induced thrust on the plate. The general procedures and working equations have been given elsewhere.[1]

Measurements were limited at high shear rates by a flow instability which, beyond a rather well-defined shear rate, causes the sample to exude from the plate–cone gap.[11,12] This phenomenon seems to develop when $p_{11} - p_{22}$ becomes comparable in magnitude to p_{12}. It also depends on apparatus geometry, particularly the cone angle. Table II shows critical shear rates $\dot\gamma_c$ (visually estimated) for the two cone angles. The ratio of critical shear rates was approximately equal to the inverse ratio of cone angles (4.0/0.583 = 6.85) in all cases. Presumably a greater penetration into the non-Newtonian region would have been possible if even smaller cone angles had been employed.

TABLE II
FLOW INSTABILITY IN PLATE–CONE VISCOMETER AT DIFFERENT CONE ANGLES

Polymer sample	Solution concn, g/ml	Shear rate at instability, sec^{-1} α = 0.583°	α = 4.0°
B6	0.260	3.67	0.427
F4	0.171	292	67.7
F4	0.260	36.7	8.49
F8	0.171	18.5	2.69
F8	0.260	2.33	0.536
F9	0.171	9.25	1.35
F9	0.260	1.46	0.269
F10	0.171	5.82	0.677
F11	0.171	3.67	0.427

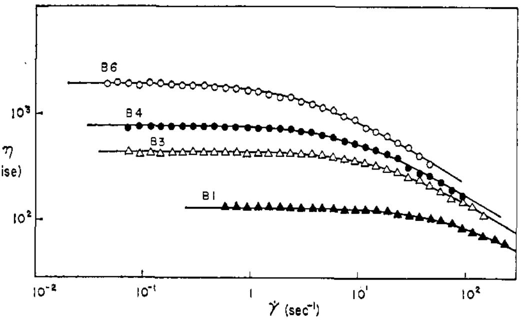

Figure 4. Viscosity *vs.* shear rate for several unfractionated (B series) poly(vinyl acetates) (c = 0.171 g/ml): ——, theoretical master curves[13] for $M_w/M_n = 2.0$ ($Z = 0$ in the Zimm-Schulz distribution).

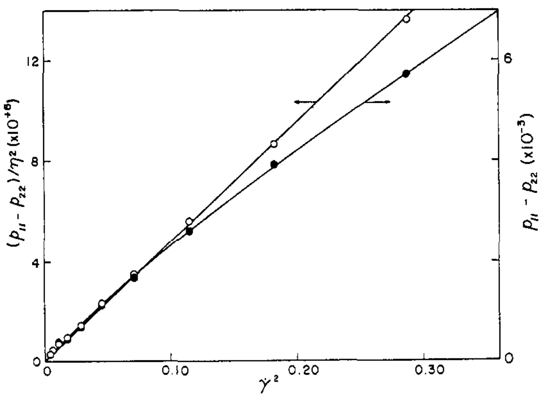

Figure 5. First normal stress difference as a function of shear rate for fraction F8 (c = 0.26 g/ml).

Viscosities for several of the solutions are shown in Figures 3 and 4 as functions of shear rate. Examples of the normal stress data are shown in Figures 5 and 6. The data in these latter figures are quite representative of the quality of all normal-stress data obtained.[8] Viscosities at zero shear rate and viscosity time constants were obtained by superposition on theoretical master curves as described earlier for polystyrene systems.[1] Master curves[13] corresponding to $\bar{M}_w/\bar{M}_n$ values of 1.09 (Z = 10 in the Zimm-Schulz distribution) and $\bar{M}_w/\bar{M}_n = 2.0$ (Z = 0) were used for the fractions and broad-distribution samples, respectively. Results are shown in Figure 7. The values of η_0 and τ_0 are given in Table III. Also listed in Table III are values of η_0/η_{FN}, in which η_{FN} is the viscosity calculated from an empirical equation for poly(vinyl acetate)–diethyl phthalate solutions given some years ago by Nakayasu and Fox.[14] Although some scatter is present, the errors appear to be random, with no systematic dependence on either concentration or molecular weight.

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(11) B. D. Coleman, H. Markovitz, and W. Noll, "Viscometric Flows of Non-Newtonian Fluids," Springer-Verlag, New York, N. Y., 1966, pp 73–74.

(12) J. F. Hutton, *Rheol. Acta*, **8**, 54 (1969).

(13) W. W. Graessley, *J. Chem. Phys.*, **47**, 1942 (1967).

(14) H. Nakayasu and T. G. Fox, presented at 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960; Abstracts, No. 11-I.

TABLE III
RHEOLOGICAL DATA ON POLY(VINYL ACETATE) SOLUTIONS

Sample	$\overline{M}_w$	c, g/ml	η_0, P	$(\eta_0/\eta_{FN})^a$	τ_R, sec	τ_0, sec	J_e, cm²/dyn	J_R, cm²/dyn
F4	292,000	0.171	107	1.19	0.00445	0.00787	$3.5_5 \times 10^{-5}$	3.39×10^{-5}
		0.260	1,028	1.13	0.0281	0.0432	2.0_3	2.23
F8	788,000	0.171	2,710	1.04	0.236	0.190	4.3_4	9.15
		0.260	21,600	0.82	1.59	0.930	2.3_7	6.02
		0.328	79,800	0.66	4.67	2.25		
F9	930,000	0.171	4,520	0.98	0.598	0.421	4.8_0	10.8
		0.260	51,500	1.10	4.48	2.30	2.3_6	7.10
		0.325	181,000	0.91	12.6	5.35		
F10	1,220,000	0.171	8,830	0.76	1.53	0.748	4.5_1	14.2
F11	1,390,000	0.171	20,600	1.14	4.08	1.96	5.8_0	16.1
		0.260	337,000	1.85	43.8	13.1		
B1	317,000	0.171	132	1.11	0.0059	0.0061		
		0.260	1,200	1.00	0.0356	0.0488	$5.5_5 \times 10^{-5}$	5.78×10^{-5}
		0.349	7,490	0.87	0.166	0.150		
B3	508,000	0.171	438	0.74	0.0317	0.0278		
		0.260	4,850	0.82	0.231	0.242	6.7	9.26
B4	556,000	0.171	765	0.95	0.0605	0.0572		
		0.349	46,900	0.80	1.82	1.39		
B6	725,000	0.171	1,880	0.95	0.194	0.169		
		0.260	22,400	1.12	1.52	0.977	6.9	12.7
		0.349	194,000	1.35	9.81	5.33		

[a] η_{FN} is the viscosity calculated from the empirical equation of Fox and Nakayasu.[14]

A normal stress coefficient was obtained for each solution and expressed in terms of steady-state shear compliance J_e

$$p_{11} - p_{22} = \theta(\dot{\gamma})\dot{\gamma}^2 \tag{5}$$

According to the Coleman-Markovitz analysis of slow flows in viscoelastic fluids[15]

$$J_e = (1/2\eta_0^2) \lim_{\dot{\gamma}\to 0} \theta(\dot{\gamma}) \tag{6}$$

or

$$J_e = (1/2) \lim_{\dot{\gamma}\to 0} [(p_{11} - p_{22})/\eta^2\dot{\gamma}^2] \tag{7}$$

As observed earlier and seen in Figures 5 and 6, plots of $(p_{11} - p_{22})/\eta^2$ *vs.* $\dot{\gamma}^2$ are linear to much higher shear rates than $p_{11} - p_{22}$ *vs.* $\dot{\gamma}^2$; J_e values were calculated accordingly from slopes of the former plots (Table III), but essentially the same values were obtained by careful application of either method. As in the polystyrene study,[1] small nonzero intercepts were sometimes found when $p_{11} - p_{22}$ was extrapolated to zero shear rate (Figure 6). This artifact is believed to be caused by very slight inaccuracies in the gap setting; it was largely eliminated in later experiments by careful attention to initial alignment and calibration.

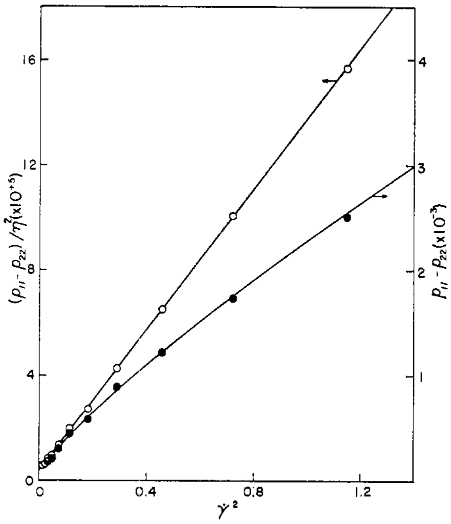

Figure 6. First normal stress difference as a function of shear rate for unfractionated sample B3 (c = 0.26 g/ml).

Discussion

Figure 8 shows η_0 *vs.* $\overline{M}_w$ for two polymer concentrations. The lines drawn have slopes of 3.4, agreeing with other studies on linear polymers[16] and likewise confirming that $\overline{M}_w$ is the proper correlating variable for viscosities in samples with different distributions. Some mild indication of a departure from 3.4 power dependence is shown by the highest molecular weight sample at c = 0.260 g/ml. This occurs at $c\overline{M}_w \approx$

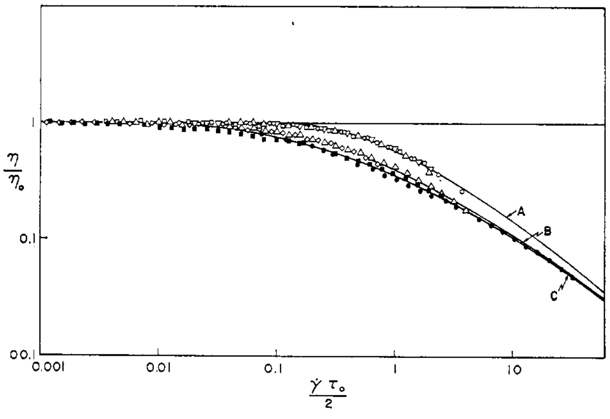

Figure 7. Viscosity master curves for poly(vinyl acetate) in diethyl phthalate: (A) data from fractions (F series), (B) data from most probable distribution samples (B series), (C) data on unfractionated branched samples reported earlier (see ref 5).

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(15) B. D. Coleman and H. Markovitz, *J. Appl. Phys.*, 35, 1 (1964).

(16) G. C. Berry and T. G. Fox, *Advan. Polym. Sci.*, 5, 261 (1968).

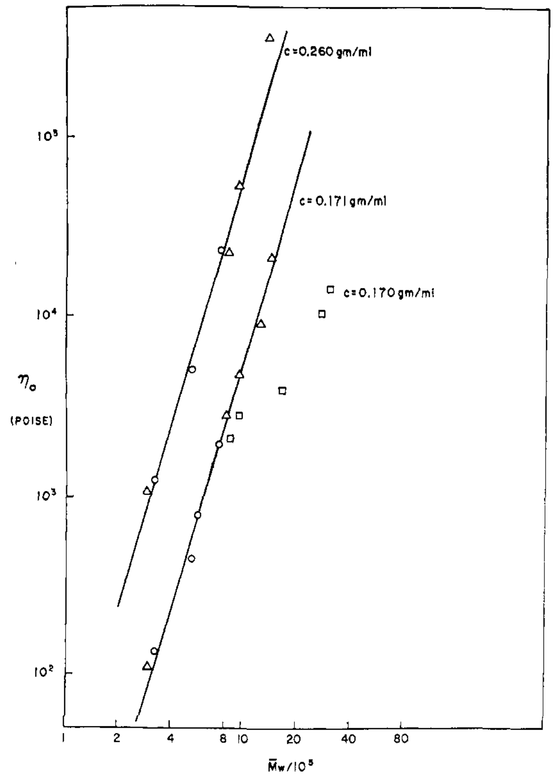

Figure 8. Viscosity *vs.* molecular weight for poly(vinyl acetate) in diethyl phthalate: Δ, data on the fractions (F series); ○, data on the most probable distribution samples (B series); ☐, data on branched samples reported earlier (see ref 5).

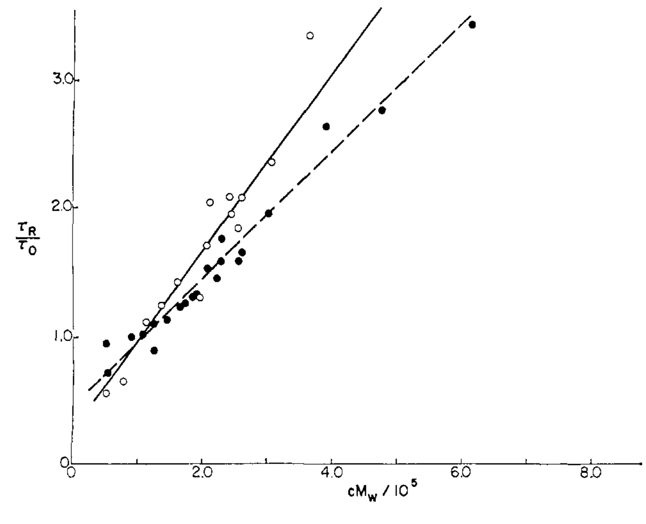

Figure 9. Viscosity time constant ratio *vs.* the product of concentration and molecular weight in narrow-distribution samples: ○, data on fractions of poly(vinyl acetate) in diethyl phthalate; ●, data on narrow-distribution samples of polystyrene in *n*-butylbenzene (ref 1) and undiluted (ref 2).

350,000, the range where others[17,18] have also observed an upturn in viscosity for linear poly(vinyl acetate). Data reported earlier[5] on a series of branched poly(vinyl acetates) are also included in Figure 8.

The relationship between the viscosity time constant τ_0 and molecular properties for the fractions is shown in Figure 9. As in polystyrene systems the ratio τ_R/τ_0 appears to be a linear function of the product cM, although apparently the polystyrene and poly(vinyl acetate) data follow slightly different paths.

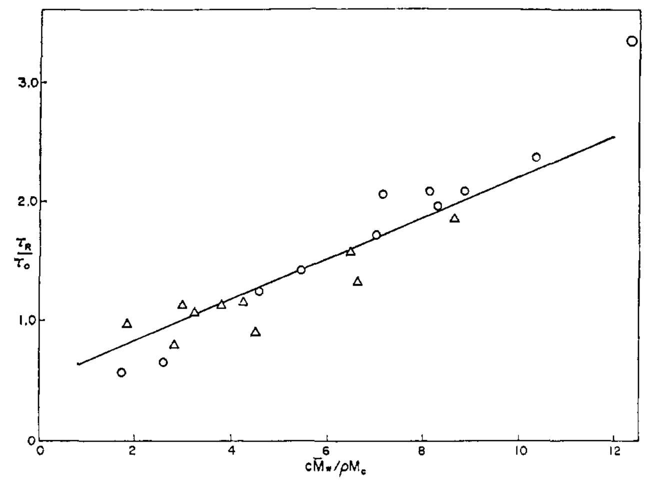

Figure 10. Viscosity time constant ratio *vs.* extent of penetration into the entanglement region: ○, data on the fractions of poly(vinyl acetate) (F series); △, data on the most probable distribution samples (B series); ——, calculated by least squares from time constant ratios on narrow distribution polystyrene (see ref 1).

Figure 10 compares the polymers at equal extents of penetration into the entanglement region. The cM products are divided by ρM_c for each polymer: densities are 1.19 and 1.07 respectively for poly(vinyl acetate) and polystyrene at 30°; the corresponding critical molecular weights M_c are 24,500 and 33,000.[10] The polystyrene results are represented by the solid line, a least-squares calculation obtained earlier.[1] Considering the uncertainty in M_c values, the agreement between the two polymers is quite good.

In the earlier study of polystyrene systems[1] the samples with narrow and exponential distributions followed the same line quite accurately. In poly(vinyl acetate) there may be some residual dependence on distribution. Careful inspection of Figure 10 shows that the fractions and the broad-distribution samples depend on $c\bar{M}_w$ slightly differently. However, the data are limited and somewhat scattered, so we are reluc-

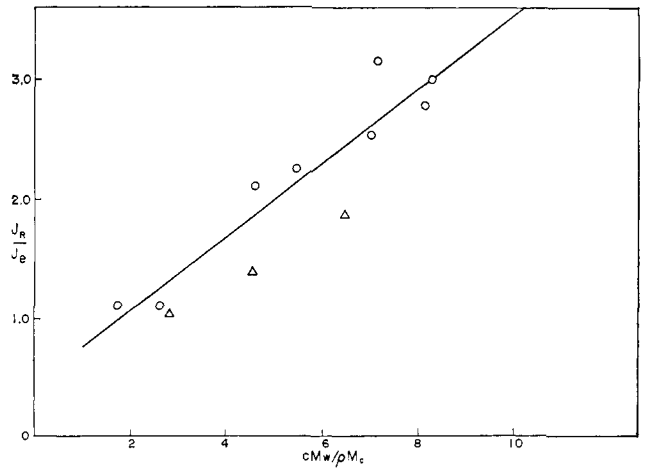

Figure 11. Compliance ratio *vs.* extent of penetration into the entanglement region: ○ and △, respectively the fractions (F series) and the most probable distribution samples (B series) of polyvinyl acetate; ——, calculated by least squares from compliance data on narrow-distribution polystyrene (see ref 1, 3, and 4).

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(17) K. Ninomiya, J. D. Ferry, and Y. Oyanagi, *J. Phys. Chem.*, **67**, 2297 (1963).

(18) S. Onogi, T. Masuda, and T. Ibaragi, *Kolloid Z.-Z. Polym.*, **222**, 110 (1968).

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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(19) W. W. Graessley, R. L. Hazleton, and L. R. Lindeman, *Trans. Soc. Rheol.*, **11**, 267 (1967).

(20) C. L. Lee, K. E. Polmanteer, and E. G. King, *J. Polym. Sci., Part A-2*, **8**, 1909 (1970).

(21) R. A. Mendelson, W. A. Bowles, and F. L. Finger, *ibid., Part A-2*, **8**, 105 (1970).

(22) J. T. Gruver and G. Kraus, *ibid., Part A*, **2**, 797 (1964).

(23) T. Fujimoto, N. Ozaki, and M. Nagasawa, *ibid., Part A-2*, **6**, 129 (1968).

(24) T. Masuda, K. Kitagawa, and S. Onogi, *Polym. J.*, **1**, 418 (1970).

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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(1) J. C. Moore, *J. Polym. Sci., Part A*, **2**, 835 (1964).