Zero Shear Viscosities of Narrow and Broad Distribution Polystyrene Melts

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ABSTRACT: This article reports results of capillary extrusion studies of four anionic and five commercial polystyrenes at temperatures between 170 and 237°. Nearly all the zero shear viscosity values recorded in the literature for narrow distribution polystyrene samples are estimated by extrapolating non-Newtonian flow data. Zero shear viscosities were obtained in the present case by extrapolation methods which are widely used in current polymer melt rheology. The differences between the estimates of zero shear viscosity (η_0) and measureable lower Newtonian apparent viscosities of fractions were not great at the relatively low molecular weights where such comparisons could be made. The choice of extrapolation method likewise seems to have had little effect on the η_0 values estimated from data in the shear-thinning regions of flow curves of narrow distribution polystyrenes. Measurements in different laboratories of the relations between η_0, molecular weight (M), and temperature agree well for polystyrene fractions. The relation between log η_0 and log M is rectilinear with a 3.4 slope in the molecular weight range studied. These conclusions do not extend to a series of broad distribution, commercial polystyrenes. Here the extrapolation method affects the estimate of η_0 strongly and large discrepancies are noted between such estimated zero shear viscosities and measured lower Newtonian viscosities. Interlaboratory agreement of η_0 values for unimodal whole polymers is decidedly worse than that noted for fractions. Although zero shear viscosities of bimodal mixtures of two sharp fractions are determined by $\bar{M}_w$ of the mixture, it appears that η_0's of broad distribution polymers are not uniquely determined by any single average molecular weight.

Viscosity–molecular weight relations of polymer melts have been studied extensively. It has been concluded that a double logarithmic plot of zero shear viscosity, η_0, against molecular weight, M, consists of two linear portions. At molecular weights less than a critical value, M_c, the viscosity is directly proportional to M and at $M > M_c$, η_0 is proportional to $M^{3.4}$.[1-3] The operative average molecular weight in this case is believed to be $\bar{M}_w$, the mean of the differential weight distribution.

Although the zero shear viscosity concept is often used without explicit definition, current theories seem to agree implicitly on η_0 as an actual or estimated lower Newtonian viscosity.

The zero shear viscosity in molecular theories is often that of an unperturbed melt. Strictly speaking, this would be the viscosity coefficient of a material with zero shear history which is subjected to vanishingly small shear stresses. These conditions are experimentally inaccessible and the utility of the concept is therefore enhanced if it is further assumed than η_0 is finite and that it is a Newtonian viscosity. Newtonian viscosity in this sense means that the apparent viscosity (ratio of corresponding point values of shear stress and shear rate) is constant over a finite range of either of these parameters.

It is necessary in continuum theories that the first derivative of apparent viscosity with respect to shear rate be zero in the limit of zero shear rate,[4] if the material is to fit the definition of a fluid. It is often also assumed that this implies the existence of a plateau viscosity region, since it would not be possible otherwise to show that the viscosity approaches a constant finite value in the limit of vanishing shear rate or shear stress.

It is expected, then, that all polymers will exhibit Newtonian viscosity regions at sufficiently low shear rates. The assumption that this constant apparent viscosity region extends from the sufficiently low shear rate mentioned to zero shear rate presumably accounts for the name zero shear viscosity. It is usually thought that η_0 depends on the polymer constitution and molecular weight and on the experimental temperature, but not on the shear history of the polymer sample.

Experimental studies of the $\eta_0 - M$ relations of polymers would be confined to rather narrow molecular weight regions if account were taken only of those η_0 values which could be demonstrated to be Newtonian viscosities. Plateau regions in plots of apparent viscosity against shear rate or shear stress have actually been measured only with fairly low molecular weight polymers. The viscosities of many of the samples in homologous molecular weight series are non-Newtonian at all conveniently accessible shear rates. In such cases η_0 is estimated by extrapolating the measured non-Newtonian viscosities to zero shear rate values. An equivalent extrapolation is required to zero frequency in the case of dynamic measurements or to steady flow conditions in stress relaxation experiments. Thus, most of the available η_0 values are estimated from non-Newtonian data. This article considers the effects of such estimation methods on η_0 viscosities of polystyrene liquids.

Polystyrene is a most attractive thermoplastic for melt rheology studies. The polymer has fairly good thermal stability, its molecular weight distribution is easily characterized and narrow distribution samples are available commercially. Considerable attention has therefore been paid to the melt flow behavior of this polymer.

The recent review of Casale, Porter, and Johnson[5] includes a summary of the most reliable $\eta_0 - M$ data for polystyrene. It is striking that no article cited in this review presents evidence that the η_0 figures reported pertained to demonstrable Newtonian apparent viscosity regions. (One table in this review includes a column listing the various methods used for extrapolation to η_0.)

Most studies of polystyrene melt rheology have involved capillary extrusion experiments in which the data were extrapolated to zero shear stress (τ) or shear rate ($\dot{\gamma}$) to provide estimates of η_0. Such extrapolations assume that a Newtonian region exists at shear rates lower than those

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in the experimental range and that the particular extrapolation method used produces estimates of η_0 which coincide with such Newtonian viscosities.

Studies with cone-and-plate rheometers usually extend to lower shear rates than those with capillary viscometers. Cone-and-plate data may appear to be Newtonian in the log viscosity – log shear rate plots usually used to summarize such observations. The log – log representation compresses the data to such an extent, however, that an apparently minor extension to what may seem to be an asymptotic value of log η_0 may correspond to a considerable extrapolation to η_0 from non-Newtonian viscosities at the experimental shear rates. (Figure 9 in the present article is an example of this.) Similar cautions apply to dynamic measurements in which log η_0 may be estimated by extrapolations to zero frequency with the usual assumption of a second-order fluid constitutive equation. Assumptions are also implicit in relaxation methods in which generalized Maxwell constitutive equations have been invoked.

This article reports a capillary extrusion study of characterized polystyrenes. Zero shear viscosities were estimated by methods used in careful studies by other workers. The low shear viscosities of some of the Pressure Chemical series of anionic polystyrenes are compared to the values for Dow narrow distribution polymers which have been reported by other workers. The $\eta_0 - M$ and η_0 – temperature relations reported here are in very good agreement with those measured by other workers with polystyrene fractions.

The η_0 values estimated with narrow distribution anionic polymers are not strongly influenced by the method used to extrapolate from non-Newtonian flow regions. Experimental lower Newtonian viscosities are slightly lower than estimated η_0 magnitudes, where such comparisons are possible. This study locates the approximate molecular weight limits at which capillary extrusion techniques cannot yield experimental Newtonian viscosities of narrow distribution polystyrenes.

The good interlaboratory coincidence of $\eta_0 - M$ results is confined to data for narrow molecular weight distribution polymers. Data on commercial, thermally initiated polystyrenes are much more scattered. The η_0 estimate in these cases is found to be very dependent on the method used to extrapolate the non-Newtonian flow data. Extrapolated η_0 values and experimental lower Newtonian viscosities may be quite different. Reasons are suggested for the differences between anionic and broad distribution polymers.

Materials. The narrow distribution polystyrene samples used were anionic polymers supplied by the Pressure Chemical Co. (Pittsburgh). Table I lists molecular weight averages provided by the supplier and $\bar{M}_v$ figures measured in this laboratory with specimens which had been extruded at some of the highest temperatures in the experimental range.[6] $\bar{M}_n$ and $\bar{M}_v$ are equivalent within experimental uncertainty for polymers with distributions as narrow as those of these samples. $\bar{M}_v$ figures were considered to be definitive since they were obtained in this laboratory on samples which had been exposed to the experimental temperatures.

Table I also lists molecular weight averages, from solution viscosity and gel permeation chromatography, of five commercial polystyrenes included in this study. The $\bar{M}_t$ values in the last column of this table are defined and discussed in a later section of this article.

Table I
Polystyrene Molecular Weights

Sample		$\bar{M}_n \times 10^{-5}$	$\bar{M}_w \times 10^{-5}$	$\bar{M}_z \times 10^{-5}$	$\bar{M}_v \times 10^{-5}$	$\bar{M}_t \times 10^{-7}$ (eq 12)
Anionic	6a	8.60[a]			7.08[7]	
Anionic	3a	4.11[a]			3.76[8]	
Anionic	4a	0.922[a]			0.892[8]	
Anionic	7a	0.510[a]			0.525[7]	
Commercial	A	0.63	2.25	5.17	2.03[9]	1.80
Commercial	B	0.69	2.60	5.05	2.35[9]	1.75
Commercial	C	0.62	3.12	6.85	2.79[9]	2.34
Commercial	D	1.26	3.02	5.35	2.92[9]	1.95
Commercial	E	1.54	3.33	5.59	3.22[9]	2.07

[a] Suppliers data.

All samples were stabilized by tumbling the polymer for at least 24 hr with 0.3% (w/w) 2,6-di-*tert*-butyl-4-methylphenol antioxidant. Previous studies[6,10] have shown that this level of stabilization is adequate.

Extrusion. The commercial polymers were extruded from a compressed gas activated capillary viscometer.[11] The cylindrical reservoir in this apparatus has a cross-sectional area of about 2 cm^2. The orifices used were drilled, flat entry tool steel dies with diameters near 0.05 cm, and various lengths. The measured gravimetric flow rates were converted to volumetric rates through use of polymer specific volumes reported elsewhere.[6]

Anionic polystyrenes were extruded from the same reservoir using a deadweight loaded piston in a technique used for simultaneous measurements of melt density and apparent viscosity.[6,12] Samples for this method were compression molded disks.[13] Orifices for this series of experiments had diameters at least double those of the dies used in the gas operated viscometer, and their length:radius ratios were considerably shorter.

Extrusions were performed at 170.1, 186.0, 204.3, 217.0, and 237.0°.

Apparent shear stresses were converted to values at the capillary wall (τ_w) by application of Bagley end corrections.[11] Corresponding rates of shear ($\dot{\gamma}_w$) at the orifice wall were obtained in the standard manner through use of the Rabinowitsch equation.[14] End-correction plots were linear for both sets of capillaries.

Polystyrene D was studied at 204.3° using both the compressed gas and deadweight piston techniques. Figure 1a shows the raw data. End-correction plots for the different capillary sets were linear, as shown in Figure 2, but the magnitudes of the end corrections differed considerably at equivalent shear rates. Despite this, the wall shear stress values (τ_w) obtained by application of these end corrections to the corresponding apparent shear stresses yield a common curve against apparent shear rate ($\dot{\gamma}_a$), as shown in Figure 1b.

Figures 3–7 show the true flow curves measured at the five experimental temperatures.

Comparison of Methods for Estimating η_0. Capillary viscometry of polymer melts rarely yields Newtonian ap-

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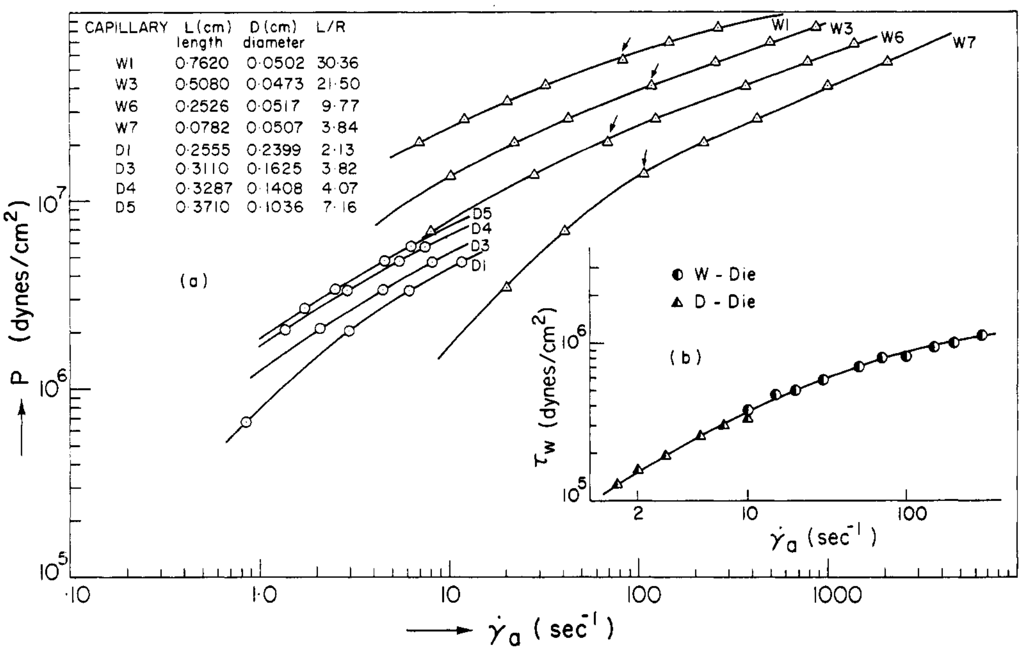

Figure 1. Polystyrene D, 204.3°: (a) extrusion pressure, P (dyn/cm^2), *vs.* apparent shear rate $\dot{\gamma}_a$ (sec^{-1}). Arrows represent the onset of melt fracture; (b) wall shear stress, τ_w (dyn/cm^2), *vs.* apparent shear rate $\dot{\gamma}_a$ (sec^{-1}).

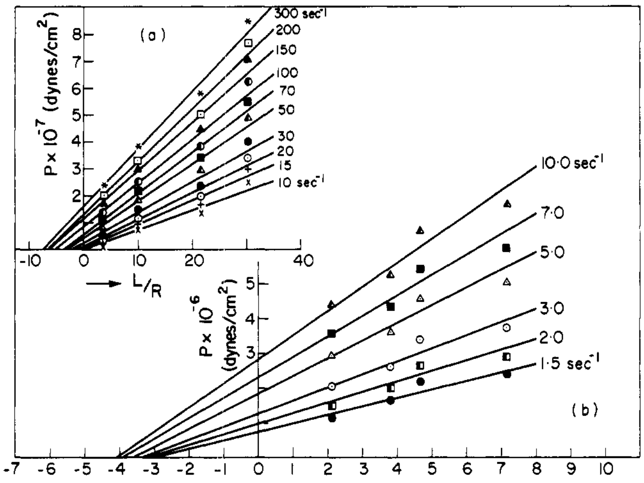

Figure 2. End correction plots of polystyrene D, 204.3°: (a) gas-operated rheometer, W capillaries (Figure 1); (b) deadweight piston rheometer, D capillaries (Figure 1).

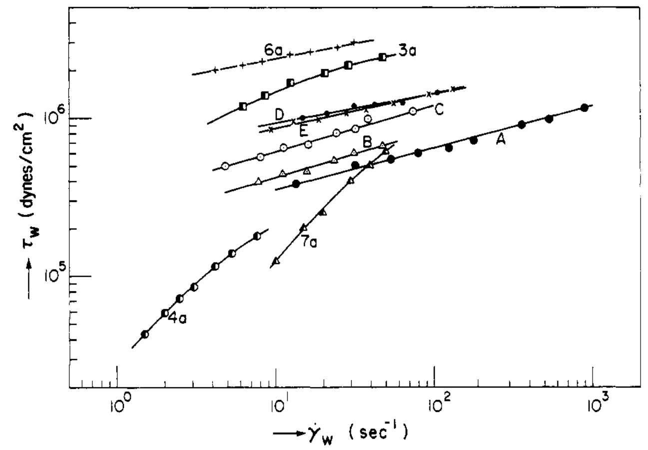

Figure 3. Flow curves, 170.1°. Symbols refer to polymer samples described in Table I.

parent viscosities of polymer melts with moderate or high molecular weights. Experimental shear thinning viscosity coefficients are usually extrapolated to zero τ or $\dot{\gamma}$ and this estimated zero shear viscosity, η_0, is assumed to be the Newtonian viscosity of the polymer.

We have commented elsewhere on some of the errors which such extrapolations can entail.[15] The uncertainties discussed below need not be important in every case, but the fact that these errors may occur makes it necessary to consider their possible significance. There is no *a priori* reason, for example, to assume that extrapolation uncertainties are independent of polymer molecular weight and extrusion temperature or even of the method used to consolidate the data for extrapolation. Detailed comparisons in subsequent paragraphs show that extrapolation uncertainties are much more serious for broad than for narrow distribution polystyrene melts. This difference could not have been forecast from superficial use of linear extrapolation estimates of η_0.

The extrapolation technique used assumes implicitly that the Newtonian region occurs only at vanishingly small shear rates. The non-Newtonian η – $\dot{\gamma}$ relation found experimentally should actually be extrapolated to the highest shear rate at which Newtonian behavior is evidenced. This shear rate is, of course, indeterminate when extrapolations are necessary. As a result, extrapolations of non-Newtonian data to zero shear rates may produce η_0 values higher than the corresponding Newtonian viscosities. These errors have been shown to be serious for some commercial polystyrenes, but not for some linear polyethylenes.[15]

The discrepancy between the extrapolated η_0 and true Newtonian apparent viscosity would be expected to decrease with increasing polymer molecular weight since higher molecular weights may be accompanied by a shift of the onset of non-Newtonian flow to lower shear rates.[16] It seems reasonable to suppose, however, that melts of polymer with sufficiently high molecular weights might

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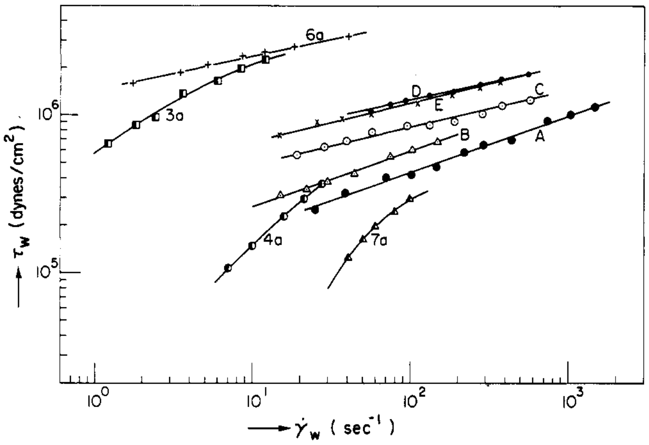

Figure 4. Flow curves, 186.0°.

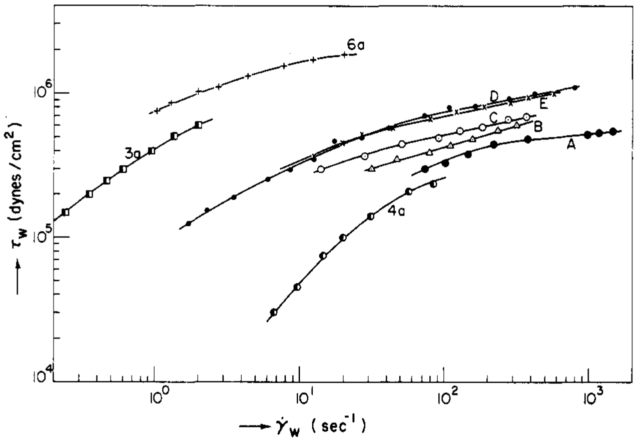

Figure 5. Flow curves, 204.3°.

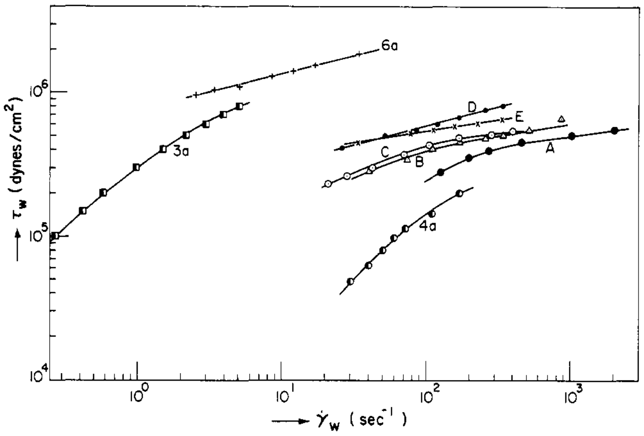

Figure 6. Flow curves, 217.0°.

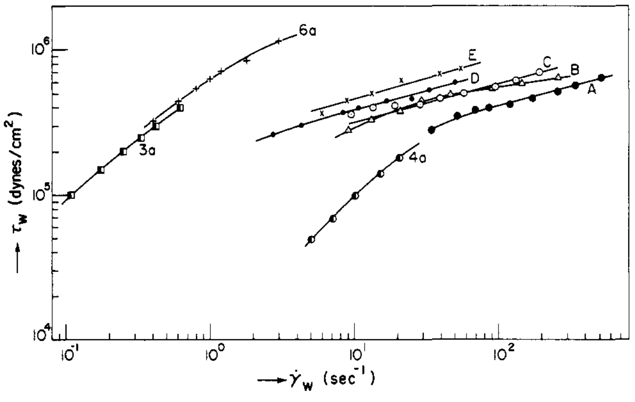

Figure 7. Flow curves, 237.0°.

have yield stresses rather than lower Newtonian regions at sufficiently small shear stresses. The extrapolation method could then err by estimating a finite η_0 when the true viscosity is infinite at zero shear rate. This error also is not detectable when the experimental data are entirely non-Newtonian.

Since flow curves of polymer melts are often curvilinear at low τ or $\dot\gamma$ direct extension of such plots to zero values of the experimental variable can be quite subjective. It seems to be better practice to convert the data to a linear form for subsequent straight line extrapolation to η_0. A number of linearization methods have been compared for this purpose.[17,18] Assessment of such techniques hinges on how well each method represents the non-Newtonian experimental points. Very few studies have considered whether such linear extrapolations actually predict experimental Newtonian viscosities. Our previous assessment with a very few samples showed better results with polyethylenes than with polystyrenes.[15] Other reported comparisons of extrapolated η_0 figures and measured Newtonian viscosities are mentioned later in this article.

In the present work, two well known extrapolation methods were found to be suitable for linearizing the experimental non-Newtonian data. One method involves plots of $1/\eta$ vs. τ_w and is based on the equation[19]

$$1/\eta = 1/\eta_0 + \tau/(\eta_0 G) \qquad (1)$$

where G has the dimensions of a modulus. This procedure has been used extensively with polyethylene melt data.[18,20,21] The second method uses the equation[22]

$$1/\eta = 1/\eta_0 + \alpha\dot\gamma^n/\eta_0 \qquad (2)$$

and involves extrapolation of $\eta^{-1} - \dot\gamma_w{}^n$ plots to zero values of $\dot\gamma_w$. In this equation α is a constant and n is a fractional index which is often, but not necessarily, equal to ⅔. The second method always yields linear plots in our experience, because of the adjustable exponent. The first method cannot always produce straight line plots.

The extrapolation techniques based on eq 1 and 2 have been examined recently in connection with polyethylene and polystyrene flow data.[15,18]

Another equation[17] which is widely used in this connection is

$$\ln\,(1/\eta) = \ln\,(A/\eta_0) + B\tau_w \qquad (3)$$

where A and B are material constants. Plots of ln $(1/\eta)$ vs. τ_w were always linear with our data but the intercepts at zero τ_w contained an unknown factor, A. Comparison with the results of extrapolations according to eq 2 indicated that A was not constant for all polystyrenes or even for the same polymer at different temperatures. Results of data treatment with eq 3 are therefore not reported here.

Transformation of experimental data to a linear form avoids subjective extrapolations to zero τ or $\dot\gamma$ for estimation of η_0 and is clearly preferable to such curvilinear extrapolations for this reason. There is no assurance in any case, however, that the polymer behavior beyond the experimental range is necessarily linear in the chosen trans-

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Table II
Estimated Newtonian Viscosities

		Fluidity – τ Extrapolation[a]			Fluidity – $\dot{\gamma}_w^n$ Extrapolation[b]			
Sample	Temp (°C)	η_0 (P)	G (dyn/cm^2)	Upper τ_w Limit to Linear Range (dyn/cm^2)	η_0 (P)	n	Upper τ_w Limit to Linear Range (dyn/cm^2)	Mean η_0 (P)
6A	170.1							
	186.0	*c*			1.96×10^7	$4/5$	2.70×10^6	
	204.3	*c*			3.02×10^6	$4/5$	1.90×10^6	
	217.0	*c*			1.75×10^6	$4/5$	1.54×10^6	
	237.0	1.06×10^6	9.70×10^5	5.0×10^6	1.05×10^6	$4/5$	0.90×10^6	1.055×10^6
3A	170.1	*c*			8.30×10^6	$4/5$	2.40×10^6	
	186.0	1.50×10^6	3.72×10^5	2.00×10^6	1.10×10^6	$2/3$	2.30×10^6	1.30×10^6
	204.3	8.75×10^5	3.86×10^5	4.00×10^5	9.76×10^5	$2/3$	6.00×10^5	9.25×10^6
	217.0	*c*			5.21×10^5	$2/3$	8.00×10^5	
	237.0	1.07×10^5	6.02×10^5	4.00×10^5	1.14×10^5	$2/3$	4.00×10^5	1.10×10^5
4A	170.1	3.15×10^4	6.00×10^5	1.00×10^5	3.47×10^4	$2/3$	1.80×10^5	3.31×10^4
	186.0	1.61×10^4	1.93×10^6	3.55×10^5	1.67×10^4	$2/3$	3.55×10^5	1.64×10^4
	204.3	6.09×10^3	3.99×10^5	1.50×10^5	7.12×10^3	$2/3$	2.40×10^5	6.61×10^3
	217.0	1.75×10^3	4.00×10^6	2.0×10^5	2.00×10^3	$2/3$	3.00×10^5	1.88×10^3
	237.0	1.00×10^3	1.50×10^6	1.8×10^5	1.25×10^3	$2/3$	2.7×10^5	1.12×10^3
7A	170.1	1.33×10^4		6.7×10^5	1.33×10^4	$2/3$	6.7×10^5	1.33×10^4
	186.0	3.52×10^3		3.0×10^5	3.52×10^3	$2/3$	3.0×10^5	3.52×10^3
E	170.1	*c*			1.30×10^6	$4/5$	1.50×10^6	
	186.0	*c*			8.50×10^5	$4/5$	1.40×10^6	
	204.3	*c*			1.89×10^5	$4/5$	1.00×10^6	
	217.0	*c*			4.09×10^4	1	6.50×10^5	
	237.0	*c*			3.32×10^4	$4/5$	7.50×10^5	
D	170.1	*c*			2.00×10^6	$4/5$	1.45×10^5	
	186.0	*c*			3.39×10^5	$4/5$	1.00×10^6	
	204.3	3.15×10^5	3.76×10^4	4.00×10^5	2.23×10^5 2.44×10^5	$2/3$ $4/5$	7.00×10^5 1.10×10^6	2.33×10^5
	217.0	*c*			6.80×10^4	$4/5$	8.00×10^5	
	237.0	*c*			3.66×10^4	$4/5$	6.00×10^5	
C	170.1	*c*			4.62×10^5	$4/5$	8.50×10^5	
	186.0	*c*			2.89×10^5	$4/5$	1.25×10^6	
	204.3	*c*			1.04×10^5	$4/5$	7.00×10^5	
	217.0	*c*			5.00×10^4	$4/5$	4.50×10^5	
	237.0	*c*			1.92×10^4	$4/5$	7.00×10^5	
B	170.1	*c*			2.98×10^5	$4/5$	6.70×10^5	
	186.0	*c*			2.25×10^5	$4/5$	7.00×10^5	
	204.3	*c*			3.35×10^4	$4/5$	6.00×10^5	
	217.0	*c*			3.19×10^4	$4/5$	6.50×10^5	
	237.0	*c*			1.57×10^4	$4/5$	6.50×10^5	
A	170.1	*c*			2.63×10^5	$4/5$	1.10×10^6	
	186.0	*c*			5.91×10^4	$2/3$	1.10×10^6	
	204.3	*c*			1.98×10^4	$4/5$	4.50×10^5	
	217.0	*c*			8.36×10^3	$4/5$	4.50×10^5	
	237.0	*c*			5.21×10^3	$4/5$	5.00×10^5	

[a] Equation 1. [b] Equation 2. [c] Data not linear in this representation.

formation function. It is further not necessary that different functions which linearize a given set of experimental points need extrapolate to the same η_0. It is quite possible, also, that extrapolations from data in different regions of τ or $\dot{\gamma}$ might all be linear and still have quite different η_0 intercepts.

The above posssibilities are illustrated below with some of the present data. We emphasize that this does not mean that our results are more uncertain than those of preceding workers. (Our data are shown below to be very close to those from other recent studies of polystyrene fractions.) The present report differs from preceding work in that it gives explicit attention to the significance of the potential extrapolation errors. Any doubts which may be raised regarding the validity of the present η_0 figures must apply equally to all studies in which η_0 is estimated by extrapolation from non-Newtonian results. This seems to include *all* current reports on $\eta_0 - M$ relations for polystyrene melts.

Figure 8a shows a fluidity – τ_w plot (eq 1) of whole polymer D data at 204.3°. The low shear stress region ($\tau_w \leq 4.0 \times 10^5$ dyn/cm^2, triangles) data points are linear and extrapolate to give an estimated η_0 of 3.15×10^5 P. It is evident here, however, that the four or five lowest shear stress values recorded as circular data points are also fairly linear. This latter group is in the range $4 \times 10^5 < \tau_w < 7 \times 10^5$ dyn/cm^2. If the experimental range had included only $\tau_w \geq 4 \times 10^5$ dyn/cm^2 a much higher η_0 would have been estimated by the same extrapolation technique. For this polymer at least, the Newtonian viscosity estimated with eq 1 depends on the experimental shear stress range on which the extrapolation is based.

Figure 8b shows a fluidity – $(\dot{\gamma}_w)^{2/3}$ plot for the sample D data obtained at $\tau_w \leq 7 \times 10^5$ dyn/cm^2 (eq 2). The

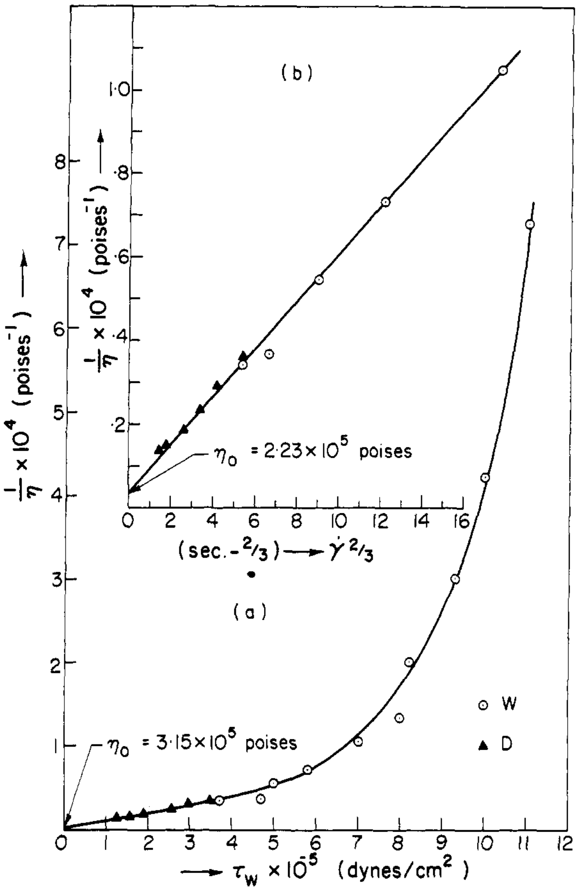

Figure 8. Sample D, 204.3°: (a) fluidity – shear stress plot; (b) fluidity – $(\dot{\gamma})^{2/3}$ plot.

data are linear in this representation and yield an estimated η_0 of 2.23 × 10^5 P. In this case, also, a plot (not shown) of $1/\eta$ *vs.* $(\dot{\gamma}_w)^{4/5}$ is linear for $7 \times 10^5 \le \tau_w \le 1 \times 10^6$ dyn/cm^2 and extrapolates to η_0 = 2.44 × 10^5 P. This representation (with index, *n*, of eq 2 adjusted to make the data points linear) seems to yield intercepts which depend less on the portion of the experimental flow curve which serves as the basis for the extrapolation.

In this one example η_0 is estimated to range between at least 2.23 × 10^5 and 3.15 × 10^5 P. These estimates are based on the same data and differ only in the linearization techniques employed before extrapolation. There is no clear reason to prefer one technique over the other when each condenses the data into a linear form. There is also no evident reason from these data alone to suppose that one or other (or either!) η_0 is more representative of the behavior of the polymer at zero shear rates.

Table II lists the η_0 values obtained in this study. The results of extrapolations according to eq 1 and 2 are recorded, as are the shear stresses at which the respective data representations were no longer linear. Comparisons of the η_0 values produced by the two extrapolation methods are limited because eq 1 did not always give linear plots with the present data. Where linear extrapolations were possible with both techniques, the estimated η_0 values are seen to agree fairly well (to within about 25%) for the narrow distribution polystyrenes.

We see below that the η_0 – molecular weight and η_0 – temperature values reported here for narrow distribution polymers coincide with those given by other workers who used different anionic polystyrenes, viscosimetric methods, and extrapolation techniques. This coincidence and the agreement noted in Table II for the different extrapolation methods indicates that these data handling techniques have relatively little influence on the extrapolated η_0 figures for *polystyrene fractions.*

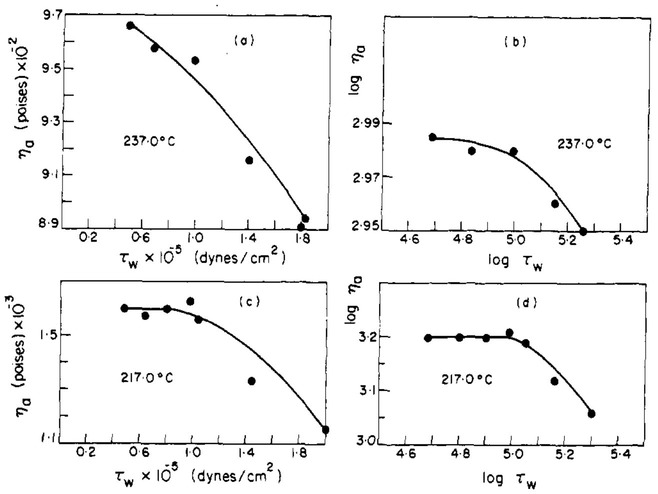

Figure 9. (a) Apparent viscosity – shear stress plot, sample 4a, 237.0°; (b) log η – log τ plot, 237.0°; (c) η – τ plot, 217.0°; (d) log η – log τ, 217.0°.

This convenient conclusion does not extend to broad distribution polystyrenes. The example given above for whole polymer D shows that the effects of a particular extrapolation method may be quite unpredictable. A similar conclusion was reached in a previous study of these two extrapolation techniques with other *broad distribution polymers.*^{15}

Comparison of Estimated and Experimental η_0 Values. The preceding section compared η_0 estimates from different extrapolation methods, so far as the available data allowed. In this section we consider how well such estimated η_0's coincide with experimental Newtonian viscosities. This comparison is restricted, of course, to cases in which experimental lower Newtonian apparent viscosities have been measured.

The capillary extrusion flow curve for sample 4a had a Newtonian region at 217.0°, but not at 237.0°. The data are shown in Figure 9, where it can also be seen that a log – log representation can be misconstrued as indicating a Newtonian relation (compare Figures 9a,b). At 217.0°, the extrapolated η_0 values (Table II) are somewhat higher than the measured value, which is 1.60 × 10^5 P. This is because the extrapolation method assumes that the η_0 region is not reached until zero values of τ_w. The discrepancy is as great as 25% of the measured η_0, depending on the extrapolation method used with this sample.

Sample 7A flow curves had Newtonian regions at all experimental temperatures. The measured η_0 values, in poises, with the corresponding temperatures were: 1.33 × 10^4 (170.1°), 3.52 × 10^3 (186.0°), 8.30 × 10^2 (204.3°), and 3.30 × 10^2 (217.0°). The last two quantities listed were measured with a single capillary only, and are perhaps not true viscosities. Extrapolations at 170 and 186° yield somewhat higher figures than the measured η_0 values, as expected. These extrapolated values are omitted from Table II.

The discrepancies between estimated and measured η_0 values thus seem to be small or moderate for narrow distribution polystyrenes. The experimental comparison is restricted to polymers with molecular weights ≤100,000 which had demonstrable Newtonian viscosities under our conditions. In these cases and in a previous comparison of several linear polyethylenes^{15} the estimated η_0 is greater than the experimental Newtonian viscosity.

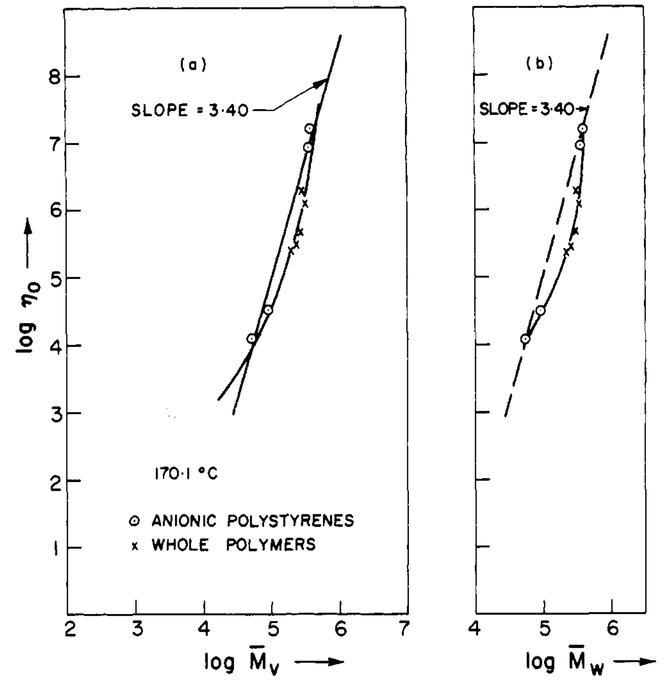

Figure 10. Zero shear viscosity – molecular weight plots, 170.1°.

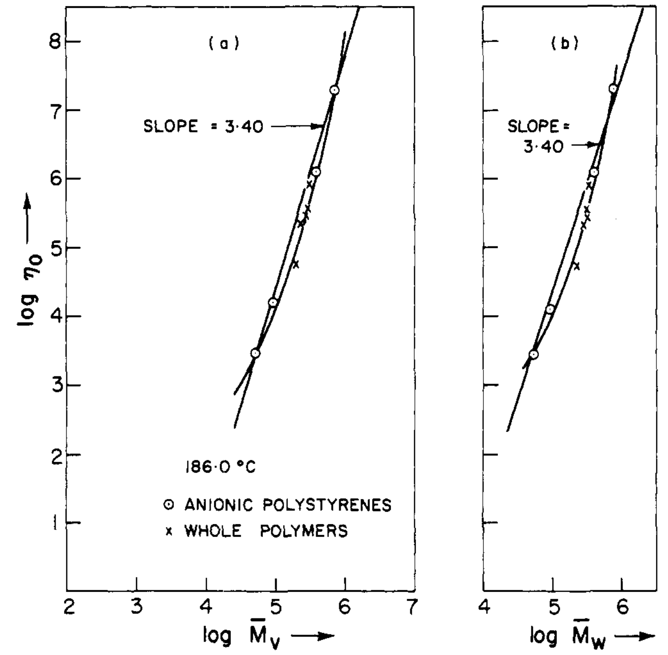

Figure 11. Zero shear viscosity – molecular weight plots, 186.0°.

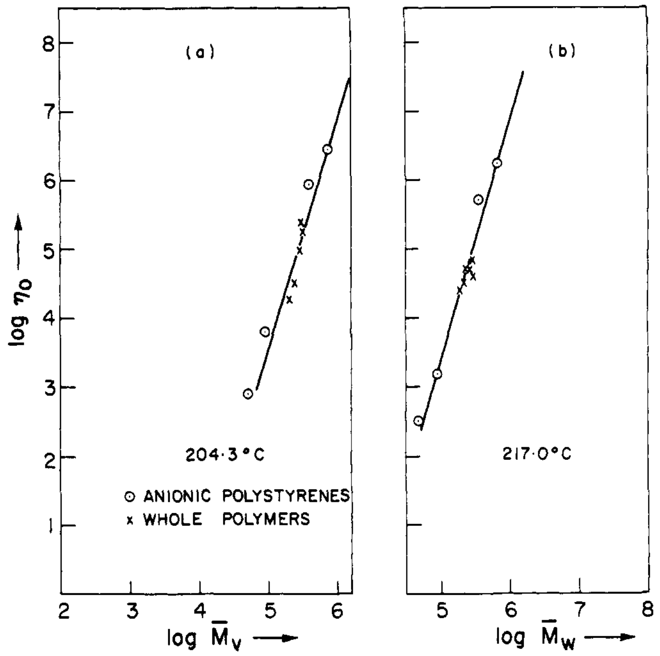

Figure 12. Zero shear viscosity – molecular weight plots: (a) 204.3°; (b) 217.0°.

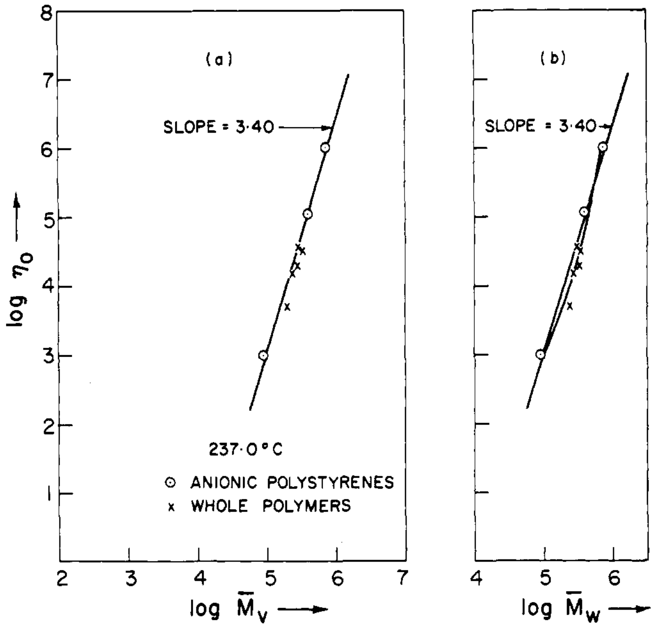

Figure 13. Zero shear viscosity – molecular weight plots, 237.0°.

The behavior of whole polymers is different from that of fractions in this comparison as it was in the preceding section of this article. Experimental Newtonian viscosity regions were not seen in the capillary flow curves of any of the commercial polystyrenes studied here. All the η_0 figures quoted in Table II for samples A-E inclusively are results as indicated of extrapolations to zero τ_w or $\dot{\gamma}_w$. Samples B and D have been examined before, however, at 186° with a falling coaxial cylinder viscometer and at lower shear stresses than those attained in the present work. Lower Newtonian viscosities were measured in these coaxial cylinder studies and it is instructive to compare these experimental values with the η_0's estimated by extrapolation of the present capillary extrusion flow curves.

The experimental Newtonian viscosities from falling coaxial cylinder measurements were 3.2×10^5 P for polymer B[23,24] and 1.07×10^6 P for polymer D. The corresponding η_0 values estimated from capillary viscometer flow curves are listed in Table II as 2.25×10^5 and 3.39×10^5 P, respectively. The extrapolations thus provided rather poor estimates of the experimental Newtonian viscosities in these two cases.

The falling coaxial cylinder viscometer flow curves reported elsewhere[15] for polymer D included both the Newtonian and the initial shear-thinning regions. It was shown that extrapolations from the non-Newtonian portions of the flow curve did not give reliable estimates of the Newtonian viscosity. These flow curves, which extended to shear rates as low as about 10^{-2} sec^{-1} did not extrapolate

(23) K. K. Chee and A. Rudin, *Polym. Eng. Sci.*, 11, 35 (1971).

(24) K. Sato, A. Rudin and K. K. Chee, *Can. J. Chem. Eng.*, 50, 576 (1972).

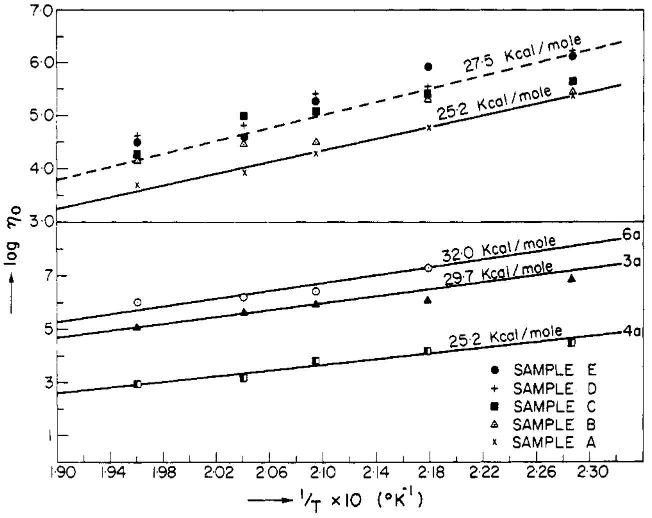

Figure 14. Arrhenius plots for zero shear viscosity.

to the same η_0 intercepts as those obtained from the present capillary extrusion flow curves at shear rates ≥ 1 sec^{-1} (Figure 4).

We see, then, that the η_0 intercepts obtained by extrapolations of linearized non-Newtonian flow data of broad distribution polystyrenes may depend on the experimental shear rate region. The deviations between estimated η_0's and experimental Newtonian viscosities may be large and unpredictable.

η_0 − M Relations. Figures 10-13 show the log η_0 − log M relations obtained at the various experimental temperatures. In these plots η_0 is always the mean extrapolated zero shear viscosity listed in Table II and M is either $\bar{M}_v$ or $\bar{M}_w$, as indicated. (The data points for polymer 7A are included in Figure 12, but not in Table II. These values were obtained with a single capillary only.) The expected 3.4 slope of the log − log plot is also shown. It is seen that the narrow distribution polymer data (three or four points) can be represented quite well by the "standard" line. When the five data points for the whole polymers are included, however, the overall relation is curved, with the radius of curvature of the log − log plot decreasing with increasing extrusion temperature.

Arrhenius plots of η_0 for the experimental temperature range are shown in Figure 14. The activation energies for zero shear viscosity are marked on the plots. The values obtained lie well within the range of reported activation energies summarized by Casale, Porter, and Johnson.[5] There appears to be a trend (which may be an artifact of the particular data) for the activation energy to decrease with decreasing $\bar{M}_w$ and to level off at about 25 kcal/mol at $\bar{M}_w$ near 200,000. This activation energy coincides with results of a careful analysis of rheological measurements on the Dow series of polystyrenes, which have molecular weights up to about 200,000.[5]

Narrow Distribution Polymers. There is considerable scatter in literature values of the η_0 − M relation.[5] Our results lie about in the center of the reported spread. The least cluttered comparison with literature data seems to be against the consensus of results on Dow series of anionic polystyrenes, as reported by Rudd,[25,26] Stratton,[27] and Hagan *et al.*[28] Casale and coworkers have considered this work critically and summarized the results (shifted to 200°) as

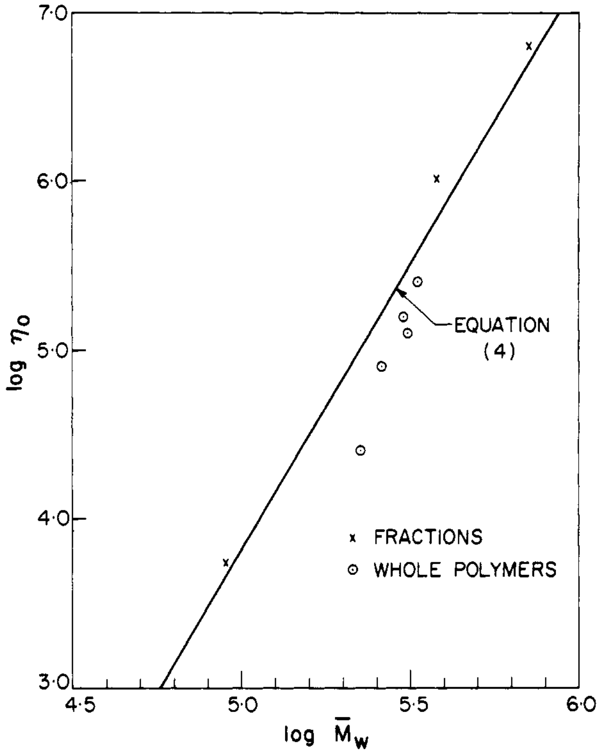

Figure 15. Present zero shear viscosity − molecular weight at 200° compared to relation of eq 4.

$$\log \eta_0 = 3.38 \log \bar{M}_w - 13.08 \qquad (4)$$

The 200° η_0 value for each polymer in our series was interpolated from the plots in Figure 14. The resulting data are compared to eq 4 predictions in Figure 15. The data for the three fractions studied in this work coincide with the predicted relation about as well as those of the cited authors.[25-28] The data for broad distribution polymers lie to the right of the log − log line. This representation is, of course, not much different from that shown in Figure 12a with a 3.4 slope at 204.3°.

The η_0 − M relations and activation energy for η_0 reported for the Dow series of narrow distribution polystyrenes[5] are seen to correspond quite well to that reported in this work from a study of Pressure Chemical anionic polymers.

A further comparison is possible with the recent results of Zosel[29] for yet a different series of narrow and broad distribution polystyrenes. In this case η_0 was derived from the measured loss modulus by assuming that a second-order fluid constitutive equation applied to the behavior of the polymer melt. Zosel gives the following relation for all polystyrenes at 190°

$$\log \eta_0 = -12.8 + 3.4 \log \bar{M}_w \qquad (5)$$

Table III compares the log η_0 values calculated from eq 5 with our corresponding zero shear viscosities read from the experimental plots in Figure 14. Attention at this point is confined to the narrow distribution polymers only. We see that the log η_0 values compare closely, although the polymer samples, molecular weight measurements, and viscometric techniques were different and independent in the two studies.

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(25) J. F. Rudd, *J. Polym. Sci.*, 44, 459 (1960).

(26) J. F. Rudd, *J. Polym. Sci.*, 60, 57 (1962).

(27) R. A. Stratton, *J. Colloid Interface Sci.*, 22, 517 (1966).

(28) R. S. Hagan, D. P. Thomas, and W. R. Schlich, *Polym. Eng. Sci.*, 6, 373 (1966).

(29) A. Zosel, *Rheol. Acta*, 10, 215 (1971).

Table III
Experimental and Calculated η_0 Values – 190°

Sample	Experimental η_0 (P)	Experimental Log η_0	Calcd Eq 5[29] η_0 (P)	Calcd Eq 5[29] Log η_0
6a	1.26×10^7	7.10	1.20×10^7	7.08
3A	2.00×10^6	6.30	1.41×10^6	6.15
4a	9.12×10^3	3.96	10.50×10^3	4.02
7A[a]	3.52×10^3	3.33	1.78×10^3	3.25
E	5.62×10^5	5.75	9.33×10^5	5.97
D	2.51×10^5	5.40	6.76×10^5	5.83
C	2.24×10^5	5.35	7.59×10^5	5.88
B	1.0×10^5	5.00	4.07×10^5	5.61
A	4.47×10^4	4.65	2.46×10^5	5.39

[a] 186.0°.

In summary, it is clear that the $\eta_0 - M$ and temperature dependence of η_0 of narrow distribution polystyrenes reported in this article are in good agreement with those quoted in recent[5,29] studies with other polystyrene fractions. This coincidence between the results of five laboratories (Rudd,[26] Stratton,[27] Hagan *et al.*,[28] Zosel,[29] and ourselves) is unusually close, for polymer melt rheological data. It lends support to the reliability of the present experimental methods and results with all samples.

Are the η_0 Values Newtonian Viscosities? We have noted above that the η_0 figures reported here for the 50,000 molecular weight sample 7A are Newtonian viscosities. The η_0 values for the other three anionic polystyrenes studied in this laboratory are extrapolated estimates. Such estimates were compared to measured Newtonian viscosities in a preceding section of this article. Since our extrapolated η_0 values coincide with the η_0 figures given by other workers, it is interesting in this context to review whether the latter are experimental Newtonian or estimated zero shear viscosities. It turns out, as shown below, that none of the other workers whose studies of narrow distribution polymers were cited measured Newtonian viscosity regions.

We consider first the three reports[26-28] quoted by Casale and coworkers[5] on the Dow series of anionic polystyrenes. Rudd's[26,27] η_0 values are extrapolated by eye on log viscosity – log shear stress plots from non-Newtonian regions to zero shear stress. Stratton[28] stated explicitly that all his flow curves were non-Newtonian and resorted to an extrapolation procedure similar to that quoted here as equation 1. Stratton gave reasons for preferring this extrapolation method to that of Rudd, and suggested caution in interpreting the absolute magnitudes of the extrapolated η_0's. The data of Hagan and coworkers[28] are for one narrow distribution polymer at shear rates greater than 1.5 $\sec^{-1}$ and are entirely non-Newtonian.

Zosel[29] studied a different set of anionic polystyrenes in small amplitude oscillatory deformation. Second order fluid theory gives η_0 as the limit at zero frequency of the ratio G''/ω, where G'' is the imaginary part of the shear modulus at frequency ω. The estimation of η_0 depends on the assumption of the second order fluid constitutive equation and various temperature and frequency superpositions which smooth the experimental data.

This report and the other studies quoted[5,29] agree essentially on the $\eta_0 - M$ relations for narrow distribution polystyrenes at temperatures between 170 and 237°. Almost all the zero shear viscosities are estimates by various extrapolation methods. It may be argued that the coincidence of results from different laboratories shows that the estimated η_0 values are indeed real properties of the particular polymers. This reasoning is compelling, but it does not necessarily mean that the real property involved must be an observable Newtonian apparent viscosity.

We recall in this connection that the various estimation methods for η_0 which were examined above all tended to overestimate the magnitude of the experimental Newtonian viscosity to some extent. It is important to note, also, that Newtonian regions are shown to exist only for lower molecular weight polymers. By analogy, higher molecular weight species are assumed to have lower Newtonian regions under experimental conditions which are not measureable by present techniques. Conclusions reached by such analogies must reflect the initial premises. If we had reasoned, for example, from the properties of very high molecular weight polymers a similar analogy would suggest that intermediate molecular weight homologs have yield points at low shear stresses. Experimentally, we know that low molecular weight polymers have lower Newtonian flow regions and that very high molecular weight materials are Bingham-like materials. The intermediate region includes the polymers of most commercial and scientific interest. These are the materials for which η_0 values are estimated from non-Newtonian experimental data.

It would seem, in conclusion, that while the η_0 figures reported here and by the other authors quoted may be close to the magnitudes of Newtonian viscosities, the two parameters probably diverge at a sufficiently high and presently indeterminate molecular weight.

3.4 Power Law Relation. Our data and the other results quoted for polystyrene fractions fit a relation in which η_0 is proportional to $M^{3.4}$. The bulk of other reports on melt flow behavior of narrow distribution polystyrenes also give log η_0 – log M slopes of 3.4.[5] Deviations from this value are attributable in part to interlaboratory discrepancies in molecular weight measurements. A difference of 10% in M is approximately equivalent to a 35% change in η_0, with this relation.

Comparisons between different sets of experimental results have usually seemed to focus on the slopes of rectilinear log η_0 – log M plots. The intercepts in such plots (at fixed log M) seem, however, to vary rather more widely than the slopes. This may be connected with the fact that the η_0 figures of all investigators are estimates obtained by various extrapolation methods and are based on somewhat different experimental shear rate regions. The values found for η_0 may depend in part on the extrapolation method and on the region of the flow curve from which the jump to zero τ or $\dot{\gamma}$ was made.

The pioneering study of Fox and Flory[30] is a case in point. The present log η_0 – log M slope is the same as that found by Fox and Flory, but the η_0 of these authors is higher, at given M, than that of this article and the other cited studies on anionic polystyrenes. This difference is consistent with that noted elsewhere[6] for specific volumes associated with chain ends of anionic and thermally initiated polystyrenes. However, the two different polymer types are reported to give equivalent viscosities at fixed M and T.[31] Thus, the parallel displacement of log η_0 – log M lines probably reflects differences in extrapolation methods for η_0, since Fox and Flory extrapolated data from their coaxial cylinder viscometer to zero applied load on the moving cylinder.[30]

Whole Polymers. The evidence summarized above showed that the η_0 estimate is much more sensitive to the choice of extrapolation method with whole polymers than

(30) T. G. Fox and P. J. Flory, *J. Amer. Chem. Soc.*, 70, 2384 (1948).

(31) V. R. Allen and T. G. Fox, *J. Chem. Phys.*, 41, 337 (1964).

when the samples are narrow distribution polystyrenes. We have also seen that the discrepancy between η_0 estimates and the experimental Newtonian region may be much more serious in the former case. These are two reasons why $\eta_0 - M$ relations reported for commercial polystyrenes tend generally to scatter much more than those measured with fractions.

Figures 3 and 4 of ref 5 illustrate the interlaboratory scatter of $\eta_0 - M$ values for whole polymers. In these plots log η_0 is seen to increase with log $\bar{M}_w$ but the scatter is much less for narrow distribution polymers than for whole polymers. In the latter case the range of reported η_0 values is easily fourfold at molecular weights near 300,000. (The conventional log − log graphical representation tends to compress the uncertainties in the relations which have been found.)

Comparison of our results for narrow and conventional distribution polystyrene with those of Zosel[29] provides another pertinent example. As mentioned, Table III compares our log η_0 values with those calculated from $\bar{M}_w$ of the particular polymers and eq 5, of Zosel. The log η_0 values for anionic polystyrenes agree to within 3% while the corresponding values for whole polymers deviate as much as 15%. The resulting differences in η_0 values are as great as fourfold.

Another reason for the relatively poor agreement of whole polymer $\eta_0 - M$ results from different laboratories may be connected with the normalization of such data on $\bar{M}_w$ of the polystyrene. $\bar{M}_w$ has been shown to be the average molecular weight which corresponds best to η_0 of mixtures of two sharp fractions[30-32] but there are theoretical reasons to expect a relationship with an average which reflects the high molecular weight tail of the distribution more strongly than does $\bar{M}_w$.[33,34]

It may even be questioned whether any single molecular weight average should be expected to determine η_0 for all molecular weight distributions. Molecular weight averages can be measured only by experiments performed in dilute solution and extrapolated to zero concentration. These conditions are imposed in part to ensure that the polymer molecules contribute independently to the observed solution property. Molecular weight averages are never inferred from colligative properties or turbidities of even moderately concentrated solutions. It is difficult to see under these circumstances why the behavior of a melt can be expected to reflect a single average molecular weight regardless of the detailed shape of the molecular weight distribution. It seems reasonable, rather, that η_0 of a series of polymers can be related to a given molecular weight average only if the distributions to be compared are very similar.

The present η_0 data for whole polymers can indeed be reduced to a common relationship with $\bar{M}_w$. This is presumably because the molecular weight distributions of the commercial polystyrenes (Table I) do not differ greatly. This suggestion is reinforced by the evidence in Figures 10–13 that log $\bar{M}_v$ gives an even better fit than log $\bar{M}_w$ to the measured log η_0 values. The $\eta_0 - \bar{M}_v$ relation cannot be fundamental. The relation between $\bar{M}_w$ and $\bar{M}_v$ is determined by the solvent used to measure dilute solution viscosity as well as by the detailed nature of the polymer molecular weight distribution.[35]

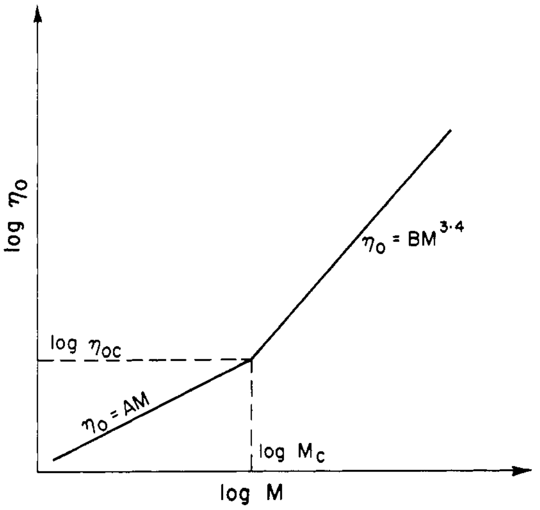

Figure 16. Schematic representation of $\eta_0 - M$ relation at fixed temperature.

Although η_0 of bimodal mixtures of fractions depends on $\bar{M}_w$,[30-32] this relation may not hold for all distribution types. Rudd's[25] measurements of η_0 for broad distribution polystyrenes scatter from the common $\bar{M}_w$ relation for narrow distribution polymers somewhat like the present data. The η_0 figure for a broad distribution polymer seems to be anomalous also in the report of Wyman and coworkers.[36] The broad distribution polymers in the latter two references and the present work are all thermally initiated bulk polymers and probably do not differ greatly in distribution shape. Conventional commercial polystyrenes can be correlated with $\bar{M}_w$ but the fit is not as close as with bimodal distributions formed by combination of two fractions. Molecular weight distributions which differ very much from these two types have apparently not been studied.

The question as to which molecular weight average (if any) defines the isothermal η_0 values of the present set of commercial polystyrenes can be pursued further with the present data. For the sake of argument, we proceed from the idealized log M − log η_0 plot shown in Figure 16, for a monodisperse polymer.

We assume that the zero shear viscosity of the whole polymer can be obtained by summing the contributions of individual species over the range of molecular weights in the sample.[37] The resulting expression is

$$\eta_0 = A\int_0^{M_c} M\phi(M)\mathrm{d}M + B\int_{M_c}^{\infty} M^{3.4}\phi(M)\mathrm{d}M \qquad (6)$$

where A, B, and M_c are defined in Figure 16 and $\phi(M)$ is the normalized weight distribution function for molecular weights.

Let the average molecular weight which determines η_0 be M_t, where this average is to be defined from the boundary conditions imposed by the relation shown in Figure 16. Then, if the bilinear log − log plot of Figure 16 applies regardless of molecular weight distribution

$$\eta_0 = AM_t \qquad M_t < M_c \qquad (7)$$

$$\eta_0 = BM_t^{3.4} \qquad M_t > M_c \qquad (8)$$

If the experimental η_0 for the whole polymer is $>\eta_{0c}$ (where η_{0c} is defined in Figure 16), eq 6 and 8 must be

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

(33) F. Beuche, *J. Polym. Sci.*, **43**, 527 (1960).

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

(35) A. Rudin, G. W. Bennett, and J. R. McLaren, *J. Appl. Polym. Sci.*, **13**, 2371 (1969).

(36) D. P. Wyman, L. J. Elyash, and W. J. Frazer, *J. Polym. Sci., Part A*, **3**, 681 (1965).

(37) S. Middleman, *J. Appl. Polym. Sci.*, **11**, 417 (1967).

equal. Then

$$M_t = \left[\frac{A}{B}\int_0^{M_c} M\phi(M)\mathrm{d}M + \int_{M_c}^{\infty} M^{3.4}\phi(M)\mathrm{d}M\right]^{1/3.4} \quad (9)$$

If $\eta_0 < \eta_{0c}$, eq 6 and 7 yield

$$M_t = \left[\int_0^{M_c} M\phi(M)\mathrm{d}M + \frac{B}{A}\int_{M_c}^{\infty} M^{3.4}\phi(M)\mathrm{d}M\right] \quad (10)$$

However, if $\eta_0 = \eta_{0c}$

$$A = BM_c^{2.4} \quad (11)$$

from 7 and 8. Equation 11 combines with eq 9 to give

$$M_t = \left[M_c^{2.4}\int_0^{M_c} M\phi(M)\mathrm{d}M + \int_{M_c}^{\infty} M^{3.4}\phi(M)\mathrm{d}M\right]^{1/3.4} \quad (12)$$

for $\eta_0 > \eta_{0c}$. On the other hand, eq 11 and 10 give

$$M_t = \left[\int_0^{M_c} M\phi(M)\mathrm{d}M + M_c^{-2.4}\int_{M_c}^{\infty} M^{3.4}\phi(M)\mathrm{d}M\right] \quad (13)$$

for $\eta_0 < \eta_{0c}$.

Equation 12 was readily tested with our samples, since gel permeation chromatograms provided details of the molecular weight distributions of the commercial polymers. M_t in these cases was not affected by the value of M_c chosen, within the reasonable range $2.5 \times 10^4 < M_c < 5.0 \times 10^4$. This is presumably because the changing integration limits compensated for variations in the magnitude of $M_c^{2.4}$ in eq 12.

The values of M_t found are listed in the last column of Table I. The average molecular weights are essentially the same for the five commercial polymers. The η_0 values given in Table II vary over about a tenfold range. There is no clear correlation between the magnitude of a given M_t and the corresponding η_0 at fixed temperature.

All the assumptions involved in the foregoing calculations are certainly not beyond question but the exercise is nevertheless a fairly orthodox experimental test of current models connecting η_0 and M. It does indicate that the zero shear viscosities of the particular whole polymers in our series are not connected to the 3.4 power of a single average molecular weight.

The present M_t values are almost 100-fold greater than the corresponding M_w figures. If the analysis has any validity at all, it points to the importance of very high molecular weight species through their influence on chain entanglement. The same calculations applied to bimodal mixtures such as those studied by Allen and Fox[31] place M_t intermediate between M_w and M_z.

Discussion

We have noted that nearly all η_0 values reported for polystyrene fractions are extrapolated zero shear viscosity estimates. The differences between such estimates and measureable lower Newtonian apparent viscosities of fractions are not great at the relatively low molecular weights where such comparisons could be made. The extrapolation method likewise seems to have had little effect on the values of zero shear viscosity estimated from data in the shear-thinning regions of flow curves of narrow distribution polystyrenes. These conclusions did not extend to a series of broad distribution commercial polymers which were studied along with narrow distribution anionic polystyrenes. The extrapolation method was seen to affect the estimate of η_0 strongly and large discrepancies were noted between such estimated zero shear viscosities and measured Newtonian viscosities of the commercial, unimodal polymers.

Measurements in different laboratories of the relations between η_0, molecular weight, and experimental temperature agree well, for narrow distribution polymers. The relation between log η_0 and log M is rectilinear, with a 3.4 slope, in the molecular weight range studied. The same relation appears to apply to bimodal mixtures of two sharp fractions.

Interlaboratory agreement of η_0 values for unimodal whole polymers is decidely worse than that noted for fractions. This is partly for reasons given above and partly perhaps also because the results in the latter cases are normalized on $\bar{M}_w$. It is suggested that zero shear viscosities of broad distribution polymers probably depend on the shape of the whole molecular weight distribution, rather than on a single average.

It was also concluded that the η_0 figures reported here are probably close to the magnitudes of the corresponding lower Newtonian viscosities of the particular polystyrene fractions which were studied. The physical significance of η_0 estimates with higher molecular weight polystyrenes is not entirely certain, however, and it may be expected that η_0 and Newtonian viscosity values will differ significantly at sufficiently high polymer molecular weights.

It might be thought that any question regarding the physical interpretation of η_0 has been settled by measurements[38,39] in which η_0 has been related to diffusion coefficients and hence to Newtonian viscosities of particular polymers. Because of experimental difficulties, however, such studies are confined to systems with viscosities which are less than those measured here for the lowest molecular weight materials. The physical significance of η_0 values of polystyrene melts with $M \gg 100{,}000$ is thus still open to experiment.

A recent report of Saeda and coworkers compares $\eta_0 - M$ data for fractions and whole linear polyethylenes,[40] with results generally similar to those found here for polystyrenes. Examination of the results given in this article[40] shows that flow curves of the whole polymers are decidedly non-Newtonian in the experimental range ($\dot{\gamma} > 10^{-2}$ sec^{-1}). Experimental apparent viscosities (at 190°) of fractions are also not Newtonian when the polymer molecular weight approaches 100,000. The $\eta_0 - M$ relation for fractions falls on a straight line with slope 3.42, but a common relation is not obtained if M is equated also to $\bar{M}_w$ of whole polymers.

Onogi and coworkers[41,42] report that slopes of the log M_w − log η_0 relation for poly(methyl methacrylate) are different for various fractions and blends. The same group finds a common relation (with some scatter) for blends and narrow distribution polystyrenes at 160°.[43,44] The slope reported is, however, 3.7 in the usual log − log plots. These results, from dynamic measurements, predict considerably higher η_0 figures for high molecular weight polymers than the values given by the conventional 3.4 slope from capillary measurements. The latter, lower viscosities pertain to materials which have been subjected to more

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pronounced shear histories in the capillary instruments and it is possible that the η_0 estimates in the two cases are derived by extrapolation from behavior of polymers in different rheological states.

Cantow[45] studied bulk polymerized polystyrenes at 217° with a Haake consistometer. The η_0 values were obtained by plotting log η *vs.* $\dot{\gamma}^{1/3}$. Examination of the data given shows that η_0 varies with $\bar{M}_w$, as in our study and others quoted, but the agreement is not close compared to that found with fractions and blends of fractions.

Schreiber, Bagley, and West[21] compared extrapolated η_0 values and experimental Newtonian viscosities of fractionated linear polyethylenes. Their conclusion that the two parameters agreed well coincides with results of previous work from this laboratory,[15] in which it was reported that the encouraging behavior of polyethylene data did not extend to whole polystyrene polymers. There is thus no disagreement between the present conclusions and those of the cited authors.[21]

Schreiber and coworkers found a 4.22 slope in log $\bar{M}_w$ − log η_0 plots for polyethylenes. Mendelson and coworkers[46] report a 3.52 slope at 150° for a set of polyethylene whole polymers. As mentioned above, Saeda and coworkers find yet different relations for fractionated and whole polyethylenes.

Results of the studies mentioned and the present work point to the conclusion that η_0 is not necessarily a unique function of $\bar{M}_w$ for all molecular weight distributions. A correlation can certainly be established with $\bar{M}_w$ (or any other average molecular weight) over a series of polymers with similar distributions. Such a relation is illustrated in the present article. It is tempting to conclude that $\bar{M}_w$ is definitive in determining η_0 because the log η_0 − log M slope tends to be generally closer to the 3.4 value characteristic of fractions with $\bar{M}_w$ than any other average. In many cases, however, it seems that normalization on an average reflecting higher moments of the distribution of whole polymers may account for the experimental data much better than $\bar{M}_w$, even though the resulting slope deviates from the expected 3.4 value. We suggest that it is most reasonable to expect that no single average molecular weight can determine η_0 of all distributions. The question is certainly not resolved, but the weight of evidence cited tends to support this view.

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Consequences of the Excluded Volume Effect on the Rate of Reactions Involving Two Randomly Coiled Polymer Chains. I. Theoretical Study[1]

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ABSTRACT: Two theoretical models were explored to assess the effect of the attachment of two chemically interacting groups to the backbone of polymer chains on the rate constant characterizing their reaction. In the first, the polymers were represented by two spherical clouds with a uniform chain segment density. In the second, the number of nonintersecting configurations of the reagent chains and of the transition state in which they are linked by a bridge were estimated by Monte Carlo calculations and the resistance to coil interpenetration was estimated from the decrease in the number of these configurations accompanying the formation of the transition state. This approach demonstrates that the rate constant depends on the location along the polymer chain at which the reactive group is attached, but the results of the computation are not easily compared with experimental data.

The very large second virial coefficient A_2 characterizing flexible chain polymers in good solvent media bears evidence to the difficulty for any mutual interpenetration of the randomly coiled chains. It should be noted, however, that the single parameter A_2 cannot describe $\Delta G(r)$, the dependence of the change in free energy on the separation between the centers of gravity of two molecular coils. In particular, the vanishing A_2 in Θ solvents which requires $\int\{1 - \exp[-\Delta G(r)/kT]\}4\pi r^2 \mathrm{d}r = 0$ does not necessarily mean that $\Delta G(r) = 0$ for all values or r. It is quite possible that the mutually excluded volume between two chain molecules vanishes in Θ media because $\Delta G(r)$ changes sign in a manner such that positive and negative contributions to the cluster integral compensate each other and computer simulation studies seem to indicate that this is, indeed, the case.[3a]

It is, therefore, desirable to search for alternative methods which could characterize the mutual interpenetration of molecular coils. Some years ago, Morawetz and Song[3b] suggested that one could use for this purpose studies of reaction rates involving dilute solutions containing two similar copolymers carrying a small number of reactive and catalytic chain substituents, respectively. If the coils have difficulty penetrating one another, a fraction of the interacting groups will be shielded in the interior of the coils at any given time. The reaction of the two polymers was, therefore, expected to be characterized by a second-

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