

High-Density Polyethylene Melt Elasticity—Some Anomalous Observations on the Effects of Molecular Structure

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Synopsis

The die swell behavior of polymeric melts is a manifestation of melt elasticity of these materials and is of considerable commercial as well as fundamental importance. Hence, knowledge of the effect of such molecular variables as molecular weight (MW) and molecular weight distribution (MWD) on melt elasticity is important from both commercial and basic rheological points of view. The effect of these variables on melt elasticity of broad-distribution polymers in the shear rate region of commercial interest is not unambiguously known, with most published theory and experiment being applicable to the low-shear behavior of narrow-distribution polymers and blends thereof. There is indication that die swell increases with increasing MW and broadening MWD. However, the current investigation of carefully characterized broad-distribution HDPE materials prepared specifically to examine the effects of various molecular variables on melt elasticity does not support this contention and, in fact, provides consistent evidence for the opposite result, i.e., decreasing die swell with increasing MW or broadening distribution. The various samples studied were prepared by fractionation removal or addition of component molecular species or by polymerization designed to provide systematic variation of molecular parameters. Overall MWD's of the samples were characterized, and die swell behavior was determined at 200°C over a wide shear rate region in a high L/D capillary both with and without annealing of extrudates. The results are presented showing effects of specific molecular variables.

INTRODUCTION

The melt elasticity of polymeric materials in shearing flow through a die manifests itself at the die exit in the form of an expansion of the cross-sectional area of the extrudate to a size greater than that of the die. This phenomenon has been called "die swell," "memory," "puff-up," etc., and is of considerable commercial as well as fundamental rheological importance. For example, the melt elasticity of high-density polyethylene (HDPE) during flow through a die plays a controlling role in determining the conditions for achieving desired wall thickness distributions in blow-molded bottles and in obtaining thickness, or "gauge," control in sheet extrusion for thermoforming operations. Thus, definition of the effect of molecular structural parameters on die swell, or melt elasticity, in order to best match polymer rheological properties to ultimate usage is an important commercial problem, as well as being vital to the fundamental understanding of the molecular mechanisms underlying melt rheological behavior.

Most investigations into the effects of molecular weight (MW) and molecular weight distribution (MWD) on melt elasticity in shear have concerned themselves with the low-shear "steady state" compliance J_e and have been performed on narrow fractions (or on narrow MWD anionically polymerized polymers) or blends thereof.¹⁻⁸ Theoretical treatments based on the Rouse model⁹ predict¹⁰⁻¹³ increasing J_e with increasing MW for very narrow MWD, that is, nominally monodisperse polymers, a result frequently, but not always, supported by experiment. By contrast, the theoretical predictions for polydisperse polymers that J_e is proportional to a combination of high moments of distribution¹³ expressed by $(\bar{M}_z\bar{M}_{z+1}/\bar{M}_w)$ or¹⁴ by (\bar{M}_z/\bar{M}_w) have encountered conflicting experimental results, generally obtained from blends of narrow-MWD samples. Theoretical prediction of melt elasticity dependence upon molecular structure for broad (and continuous, e.g., monomodal) MWD polymers in the shear rate range of commercial interest (and of die swell measurement capability) appears to be lacking, and published experimental data are far from consistent.¹⁵⁻²³ Moreover, serious difficulties are encountered in measuring the higher moments of MWD in these polymers. The larger part of the data which are available tends to indicate, though ambiguously, that die swell in this shear rate range increases with increasing MW and with broadening MWD.

However, because of the scarcity of systematic measurements to confirm and quantify such behavior, a series of carefully designed experiments were performed to determine the die swell behavior of HDPE, comparing samples with controlled variation of specific molecular structural characteristics. Somewhat surprisingly, these experiments did not confirm the expected trends and, in fact, consistently gave reduced die swell with broadening MWD or increasing levels of molecular weight. The results of these experiments are presented in this paper.

EXPERIMENTAL

The experiments may be divided into three groups. In the first of these, the MWD of a single commercial HDPE resin was modified by fractionation, removing or adding component molecular species. These samples are prefixed F-, and the manner of preparation of each is summarized in Table I. The 4.5% low MW removal (F-104) was achieved by Soxhlet extraction of granulated base resin in a refluxing azeotropic mixture of *n*-butanol (25% by vol) and toluene (75% by vol) at 105°C. The solution fractionations (F-106 and F-107) were performed by

TABLE I
Preparation Methods for HDPE F-Samples^a

Sample	Preparation description
F-101	commercial base resin granulated in Cumberland chopper
F-102A	base resin dissolved and reprecipitated
F-102B	base resin dissolved and reprecipitated
F-104	base resin less 4.5% low MW removed by extraction
F-106	base resin less 34% middle fraction
F-107	base resin less 5% high MW fraction
F-109	base resin plus 5% high MW fraction added
F-110	base resin plus 8% low MW and 4% high MW fractions
F-111	base resin plus 33% middle MW fraction added

^a All percentages are wt-% based on weight of original sample.

TABLE II
 Molecular Structure Data—Experimental HDPE Samples^a

Sample	$[\eta]$, dl/g	$\bar{M}_n \times$ 10^{-3}	$\bar{M}_w \times$ 10^{-3}	$\bar{M}_z \times$ 10^{-4}	\bar{M}_{z+1} $\times 10^{-4}$	\bar{M}_w/\bar{M}_n	\bar{M}_z/\bar{M}_w	$(\bar{M}_z\bar{M}_{z+1}/\bar{M}_w) \times$ 10^{-6}
F-101	1.74	16.5	187	149	320	11	8.0	26
F-102A	1.75	16.8	215	184	390	13	8.5	33
F-102B	1.71	16.4	180	131	260	11	7.3	19
F-104	1.82	24.2	210	201	—	8.7	9.6	—
F-106	1.98	13.5	258	198	380	19	7.7	29
F-107	1.41	18.5	144	84	190	7.8	5.8	11
F-109	1.95	18.2	249	206	390	14	8.3	32
F-110	1.86	13.5	240	197	370	18	8.2	30
F-111	1.63	19.3	135	84	200	6.9	6.3	13
G-117	2.68	14.1	263	161	300	19	6.1	18
G-120	1.75	20.1	170	147	330	8.5	8.7	28
G-121	1.60	30.7	144	98	280	4.7	6.8	19
G-122	2.75	23.0	321	196	410	14	6.1	25
G-124	2.09	9.57	165	89	180	17	5.4	9.5
G-126	1.77	12.0	156	82	150	13	5.3	8.1
G-136	2.39	17.1	261	131	250	15	5.0	13
G-180A	1.92	10.3	173	116	210	16	6.7	14
G-180B	2.89	15.0	335	222	410	21	6.6	27
G-197	—	14.5	408	195	320	28	4.8	15
G-198	—	15.4	360	183	300	23	5.1	15
G-200	—	8.4	139	78	141	16	5.6	7.9
G-201	—	9.9	171	90	55	17	5.3	8.2
P-1023	1.29	10.9	155	200	600	14	13	78
P-1024	2.19	10.9	305	272	510	28	8.9	45
P-1026	1.85	12.0	244	244	440	20	10	44
P-1030	1.09	7.60	83.4	119	240	11	14	34

^a $[\eta]$ measured in *p*-xylene, 105°C. All MW averages from GPC.

coacervative (batch) fractionation with *p*-xylene solvent and triethylene glycol nonsolvent at 125°C. Samples F-109–F-111 were prepared by dissolving portions of the base polymer and adding in solution specific amounts of the appropriate fractions previously removed from other samples.

A second group of HDPE samples, prefixed here by G-, were prepared directly by small-scale batch polymerization to provide series of resins wherein one or another molecular parameter was held constant while other parameters were varied. Specifically, polymerized samples were designed to show (1) a systematic broadening of MWD about an essentially constant weight frequency modal value (peak MW by GPC) and (2) a systematic change in MW level. Molecular parameter data for these, as well as for the other samples discussed in this paper, are given in Table II. The third group of samples were also experimentally polymerized in a laboratory batch reactor and provide a systematic variation of molecular parameters for skewed MWD's. These latter samples are designated by the prefix P-.

Molecular characterization of these samples was obtained from intrinsic viscosity and gel permeation chromatography (GPC) measurements. The former were performed in *p*-xylene at 105°C using Cannon-Ubbelohde dilution viscometers. GPC data were obtained using a Waters Model 200 GPC instru-

ment with a series of four columns (nominal pore size 10^7 , 10^6 , 10^4 , and 10^3 Å) having a plate count of 730 plates/ft. The solvent was 1,2,4-trichlorobenzene, and the operating temperature was 135°C. Calibration of this system with narrow fractions of HDPE whose MW's were independently measured (by osmometry and light scattering) has previously been described.^{24,25} Further calibration was provided using well-characterized narrow-MWD polystyrene (anionically polymerized) samples supplied by Pressure Chemicals Co. and treating the data in terms of a "universal calibration curve," in the widely described manner.²⁵⁻²⁸ Moreover, column performance and MWD reproducibility were frequently checked by rerunning wide distribution commercial HDPE samples. As indicated earlier, various MW averages are summarized for all samples in Table II. Perhaps more significant than these averages, however, are the detailed MWD curves which will be discussed later and are grouped together in subsequently referred-to figures to compare specific samples.

The melt rheological behavior of these materials in shear was investigated using an Instron capillary rheometer. All samples to be tested were stabilized with Ionol and were compression molded and cut up into pellets of appropriate size for use with the rheometer. Extrusion rheometry was performed at 200°C with a capillary whose nominal dimensions were 0.05 in. (diameter) \times 2.0 in. (length) \times 90° (entry angle), $L/D = 40$. For this long capillary, end-effect pressure drop contributions are essentially negligible, and no end corrections to the calculated shear stresses were made. Moreover, for the purposes of this work, it appeared unnecessary to apply the usual Rabinowitsch correction to the shear rates. Thus, values of the wall shear stress and shear rate were calculated in the usual (uncorrected) manner as

$$\tau_w = RP/2L \quad (1)$$

and

$$\dot{\gamma}_w = 4Q/\pi R^3 \quad (2)$$

where P is the pressure drop along the length L of the capillary of radius R , and Q is the corresponding volumetric flow rate.

Die swell measurements were performed at various shear rates in a manner previously described.^{29,30} Briefly, the method was as follows: at a given shear rate the initial extrudate was cut off as close as possible to the die and discarded; a strand of ca. 1-1/2 in. in length was then allowed to extrude and was cut off at the die; the diameter of this extrudate was measured ca. 1/8 in. from the leading end with a micrometer and the swelling ratio B was calculated as the ratio of this extrudate diameter D_{ext} to the capillary diameter D_c ,

$$B = D_{\text{ext}}/D_c \quad (3)$$

Moreover, since previous investigations^{16,29-31} had demonstrated the necessity for annealing such polyethylene extrudates at temperatures above the melting temperature in order to attain strain-free (fully relaxed) swelling ratios, such an annealing procedure, previously described in some detail,²⁹ was used here on many of the extrudates. For the annealed extrudate, the swelling ratio is given as

$$B = (D_{\text{ann. ext.}}/D_c)(\rho\nu_i)^{1/3} \quad (4)$$

where $D_{\text{ann. ext.}}$ is the diameter of the annealed (measured at room temp.) extrudate, and the term $(\rho\nu_t)^{1/2}$ corrects the density to that of the extrusion temperature (ρ is the room-temperature polyethylene density and ν_t is the specific volume at extrusion temp.).

The swelling behavior reported in this paper is expressed either as "per cent memory" or as recoverable shear strain or shear compliance. The per cent memory is given by

$$\% \text{ memory} = (B - 1) \times 100 \quad (5)$$

where B is derived from either eq. (3) or (4) as indicated in the appropriate description of results. The derivation of average recoverable shear strain and average shear compliance (where average refers to averaging across the parabolic velocity distribution in the capillary) from annealed die swell data based on rubber elasticity theory has been given in detail elsewhere,²⁴ and only the operating equations follow:

$$S_R = \left(B^4 + \frac{2}{B^2} - 3 \right)^{1/2} \quad (6)$$

and

$$J = \frac{3}{2} \frac{S_R}{\tau_w} \quad (7)$$

where S_R is the average recoverable shear strain, J is the average shear compliance, B is the annealed swelling ratio from eq. (4), and the numerical factor in eq. (7) results from the use of the maximum, or wall, shear stress.

RESULTS AND DISCUSSION

The initial analysis of the experimental results involves attempting to correlate the die swell behavior of all samples, regardless of origin or details of MW and MWD, with specific molecular parameters, as suggested in the introductory remarks. Thus, in Figure 1 we have plotted the shear compliance J calculated

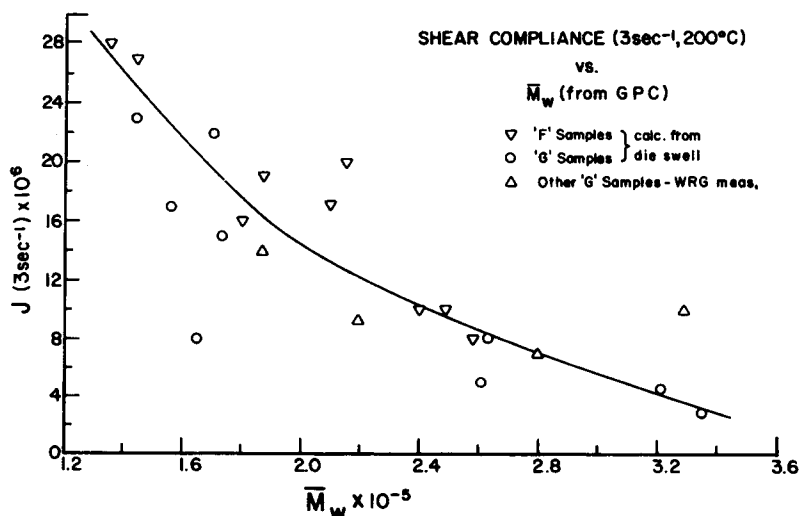


Fig. 1. Correlation of shear compliance at 3 sec⁻¹ with \bar{M}_w .

from eq. (6) and (7) from equilibrium (annealed) die swell data taken at 3 sec^{-1} shear rate against \bar{M}_w for all samples listed in Table II for which extrudate annealing experiments were performed. Also included in Figure 1 are shear compliance results obtained directly from cone-and-plate Weissenberg rheogoniom-

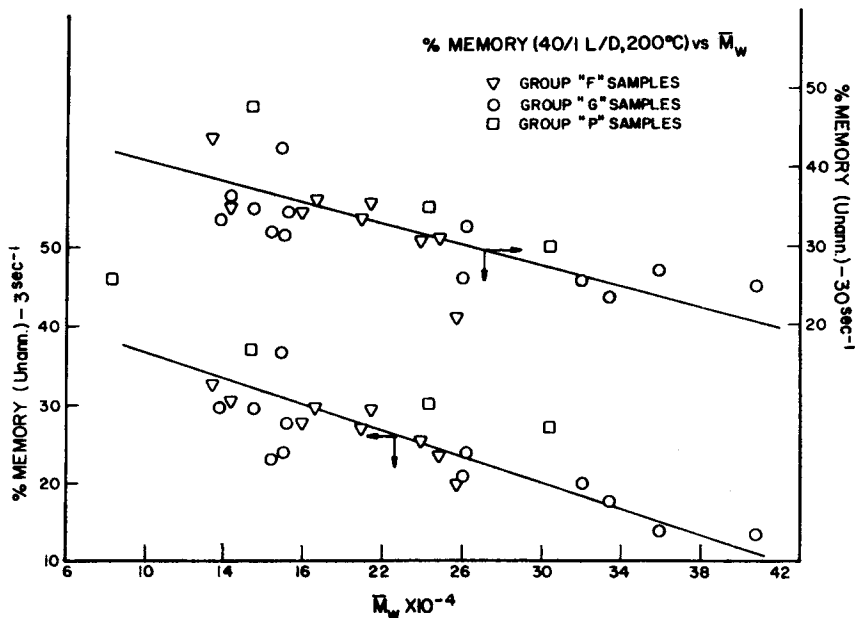


Fig. 2 Correlation of per cent memory (unannealed) at 3 sec^{-1} and 30 sec^{-1} (200°C , $0.05 \text{ in.} \times 2.0 \text{ in.} \times 90^\circ$ capillary) with \bar{M}_w .

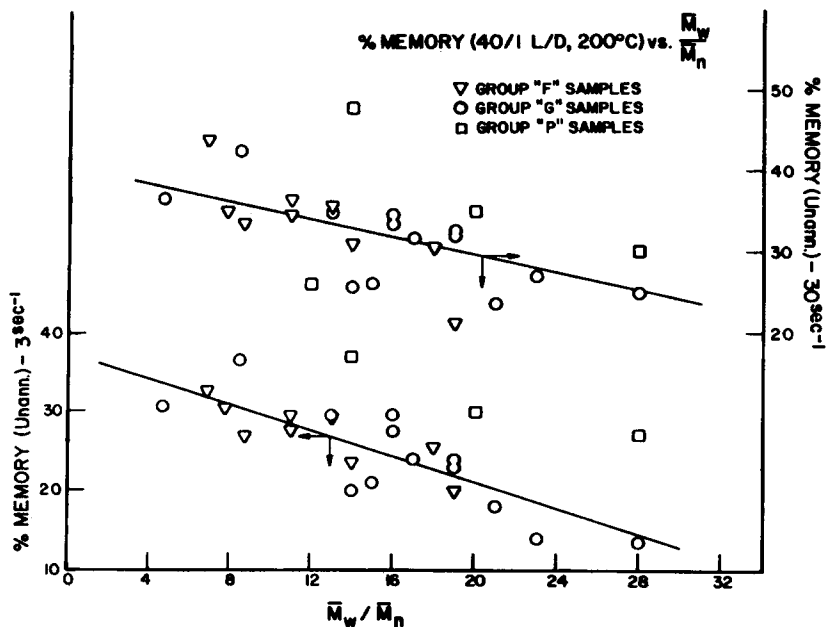


Fig. 3. Correlation of percent memory (unannealed) at 3 sec^{-1} and 30 sec^{-1} (200°C , $0.05 \text{ in.} \times 2.0 \text{ in.} \times 90^\circ$ capillary) with \bar{M}_w/\bar{M}_n .

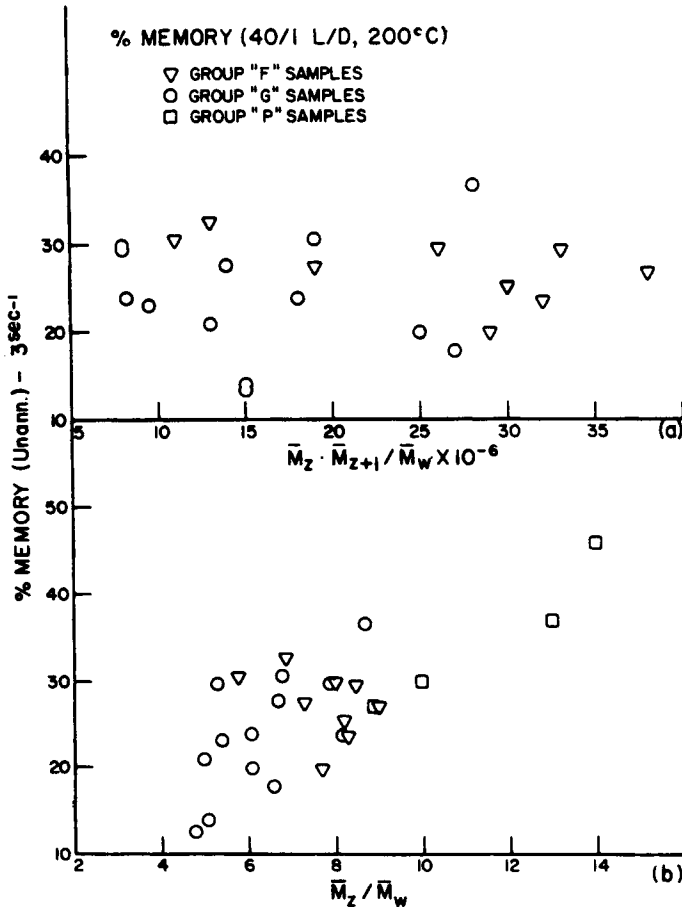


Fig. 4. Correlation of per cent memory (unannealed) at 3 sec⁻¹ (200°C, 0.05 in. × 2.0 in. × 90° capillary) with (a) $\bar{M}_z \bar{M}_{z+1} / \bar{M}_w$ and (b) \bar{M}_z / \bar{M}_w .

eter shear and normal stress measurements on four additional G-type samples, not given in Table II. Further, in a manner similar to Rogers,²² we have plotted die swell (unannealed) against (a) \bar{M}_w , (b) \bar{M}_w / \bar{M}_n , (c) $\bar{M}_z \bar{M}_{z+1} / \bar{M}_w$, and (d) \bar{M}_z / \bar{M}_w .

Figures 2 and 3 show per cent memory at both 3 sec⁻¹ and 30 sec⁻¹ for all samples plotted against \bar{M}_w and against \bar{M}_w / \bar{M}_n , respectively. Contrary to the results of Rogers, but partially in accord with Metzger and Matlack,¹⁶ memory is seen to decrease with increasing \bar{M}_w and with broadening MWD as characterized by the ratio \bar{M}_w / \bar{M}_n . Similarly, the shear compliance at 3 sec⁻¹ (Fig. 1) derived from die swell decreases with increasing \bar{M}_w , and the limited direct measurements from normal stress tend to confirm the result. In Figures 4a and 4b, respectively, the 3 sec⁻¹ memory data are plotted against $\bar{M}_z \bar{M}_{z+1} / \bar{M}_w$ and against \bar{M}_z / \bar{M}_w . In the former case, there is clearly no correlation, i.e., memory is not a function of $\bar{M}_z \bar{M}_{z+1} / \bar{M}_w$. In the latter case, the possibility of a positive correlation exists, but, with a correlation coefficient of only 0.5, it does not appear arguable that a functional dependence of memory on \bar{M}_z / \bar{M}_w exists.

The considerable scatter of the data observed in these figures is no doubt in part due to experimental error. As will be discussed later, error in \bar{M}_z and \bar{M}_{z+1}

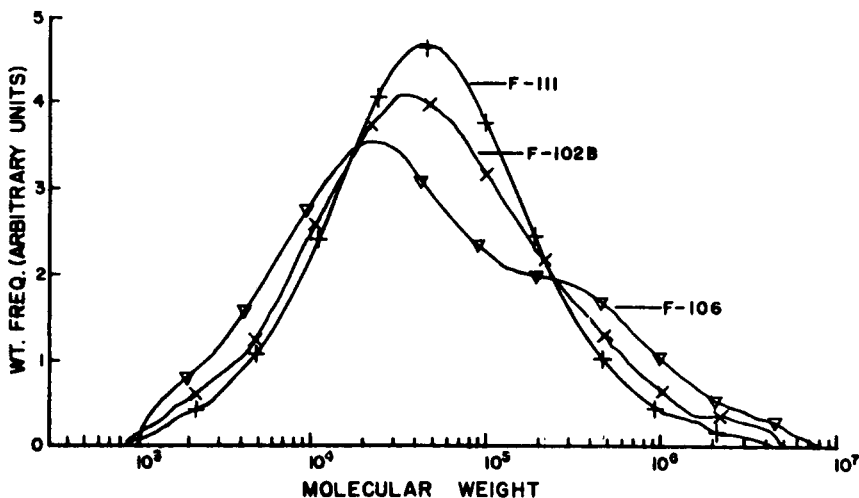
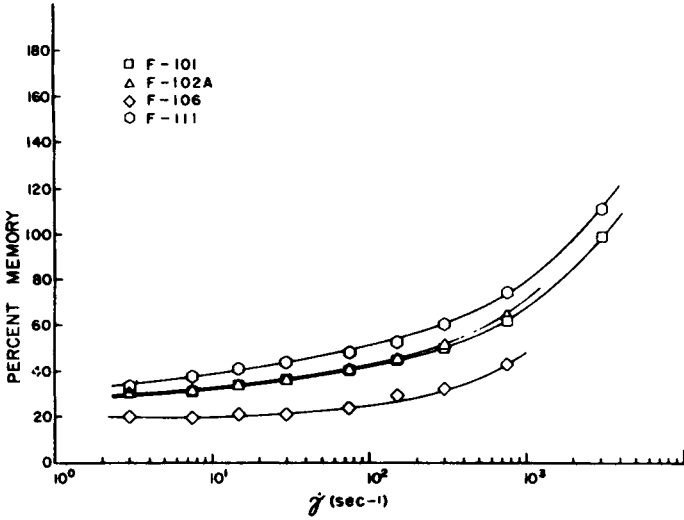


Fig. 5. Comparison of MWD curves for GPC for (×) F-102B; (∇) F-106; and (+) F-111.

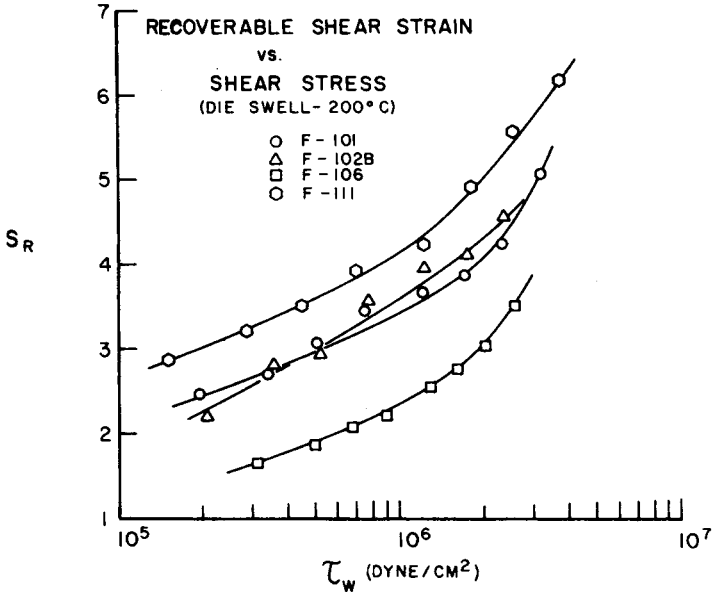
is particularly severe. However, the scatter is very likely also due to the complexity of the dependence of swelling behavior on MW and MWD breadth and shape, factors not taken into account in the simple correlation procedures described above, even though these procedures are suggested by theory. Thus, in order to ascertain the melt elasticity dependence, it is necessary to compare samples within groups prepared and selected in order to isolate as nearly as possible specific details of molecular structure. The consequences of such an approach are discussed in detail in the remainder of this paper.

Examining first the group of fractionated or reconstituted samples (F-samples), we observe from Table II that the molecular data are in accord with the method of preparation of the samples. Thus, removal of middle MW species (F-106) significantly changes and broadens the MWD shape, while adding more of these species effectively narrows the MWD (F-111). Similarly, removal or addition of high MW species (F-107) and (F-109) or addition of both sets of species (F-110) results in the expected changes in the MW averages. Two qualifications should be noted here. First, as is well known, the fractions added or removed by these methods are themselves fairly broad in distribution. Second, the higher averages, \bar{M}_z and \bar{M}_{z+1} , can be considered to be only very approximate due to the intrinsic uncertainties in the GPC method (or in any other method) in the very high MW region. However, it is significant, as will be discussed later, that reasonable correlation between \bar{M}_w , the most precisely measured average by GPC, and the higher averages was observed for most samples, suggesting that \bar{M}_z and \bar{M}_{z+1} of the samples are at least ordered correctly on a relative basis in this work.

Overall MWD curves (normalized to constant area under the curves, as are all GPC curves shown in this paper) are compared in Figure 5 for samples F-102B, F-106, and F-111, showing the large differences in MWD of these materials. Per cent memory (unannealed) data for the corresponding samples (and F-101) are shown as a function of shear rate in Figure 6a, and S_R versus shear stress data are shown in Figure 6b. First, it is quite clear that the order of increasing memory, or of increasing recoverable shear strain, is that of narrow-



(a)



(b)

Fig. 6. (a) Per cent memory (unannealed) vs. shear rate and (b) recoverable shear strain vs. shear stress at 200°C (0.05 in. × 2.0 in. × 90° capillary) for (□) F-101; (△) F-102A; (◇) F-106; (○) F-111.

ing MWD or decreasing \bar{M}_w (or higher average) over the entire range of shear rates or shear stresses investigated. Moreover, comparison of Figures 6a and 6b demonstrates that the result is the same whether the elastic response of the various materials is compared at constant shear rate or at constant shear stress. Second, the data in Figure 6a are from unannealed extrudates, as are many, if not most, of the data to be presented here, while the S_R data in Figure 6b are derived from annealed extrudates. Thus, the qualitative result, the order of change

TABLE III
 Fractionation Results—Percent Change in Memory Relative to Base Resins

Sample	Memory (unannealed)			Memory (annealed)		
	5 sec ⁻¹	10 sec ⁻¹	100 sec ⁻¹	5 sec ⁻¹	10 sec ⁻¹	100 sec ⁻¹
F-104 ^a	-10	-6	+5	-3	+1	+2
F-106	-37	-37	-38	-32	-36	-36
F-107	-7	-6	+2	0	+1	0
F-109	-20	-16	-10	-20	-23	-18
F-110	-13	-13	-12	-29	-30	-26
F-111	+17	+19	+19	+20	+12	+11

^a Sample F-104 per cent change calculated relative to base resin F-101; all others calculated relative to base resin F-102B.

with molecular structure variation, is independent of whether the die swell is measured on annealed or unannealed extrudates, a result which was found to be universally true in this work, as additional comparisons will substantiate. Third, it is notable from Figure 6 that the elastic response data for sample F-101, which was granulated directly from pellets but never dissolved or otherwise subjected to a treatment which might be expected to lead to chain disentanglement, were in excellent agreement with those of sample F-102A (prepared identically with F-102B, see Table I), which was dissolved and reprecipitated prior to compression molding and preparation for rheological measurement. This result will be discussed further at a later point.

A more complete picture of the effect on melt elasticity of manipulating the MWD's of the samples in this group may be obtained by calculating the per cent change of memory for each sample at fixed shear rates relative to the memory of the base sample at the same shear rates. This per cent change is expressed as

$$\% \text{ change} = \frac{\text{sample memory} - \text{base resin memory}}{\text{base resin memory}} \times 100. \quad (8)$$

Thus, the effects on polymer memory of changing the MW averages and MWD's are summarized in Table III as per cent change in memory at three shear rates. Both per cent change in unannealed and annealed memory are shown, confirming the earlier statement that annealed data show the same relative behavior as that of unannealed extrudates. Although base resin samples F-101, F-102A, and F-102B all show much the same memory curve (see F-101 and F-102A in Fig. 6), it was thought appropriate to calculate the memory change of F-104 relative to the granulated polymer, F-101, and the memory changes of the other samples relative to the dissolved and reprecipitated sample, F-102B. Dramatic changes in memory are reflected in Table III for four of the samples, three (F-106, F-109, F-110) showing significantly decreased memory at all shear rates with broadening MWD, and one (F-111) showing a significant increase in memory with narrowed MWD. The small changes in memory shown for samples F-104 and F-107 are probably within experimental error limits of no change. This is particularly surprising in the case of F-107, which should be expected to show an opposite and, perhaps, equal magnitude effect as that of F-109. Nonetheless, the overall picture for these samples indicates decreasing die swell with broadening MWD and/or increasing higher moment MW. It is not possible, since these molecular

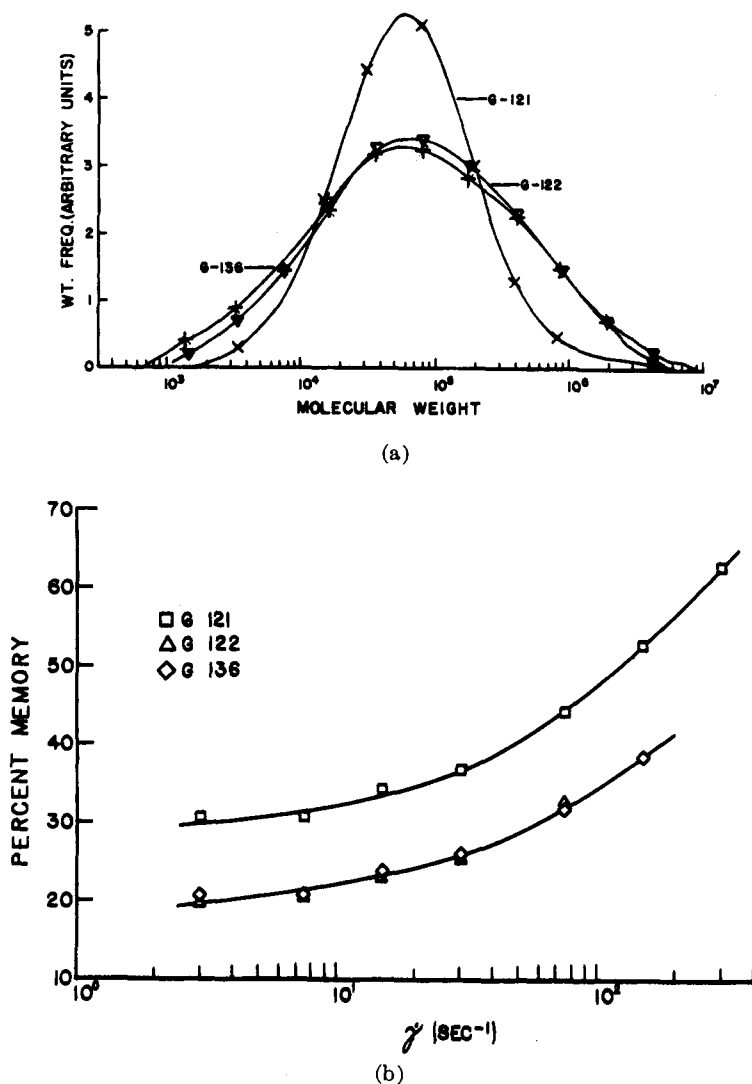


Fig. 7. (a) Comparison of MWD curves from GPC for (x) G-121, (v) G-122 and (+) G-136; and (b) per cent memory (unannealed) vs. shear rate at 200°C (0.05 in. \times 2.0 in. \times 90° capillary) for (□) G-121; (Δ) G-122; (◇) G-136.

parameters are to some extent correlated, to determine which is controlling, but in any case the result is contrary to expectation.

Turning now to the second group of samples (G-samples), we compare these in subgroups chosen to vary only certain molecular characteristics at a time. Thus, the MWD curves of three samples (G-121, G-122, G-136) are compared in Figure 7a where broadening MWD about a constant weight frequency modal value (ca. 56,000 in this case) is illustrated. Samples G-122 and G-136 are relatively similar and are very much broader than G-121. (This similarity of G-122 and G-136, in contrast to their tabulated MW averages in Table II, suggests the importance of viewing the overall distribution curve rather than relying totally on the calculated averages.) The effect of the variation in breadth of distribu-

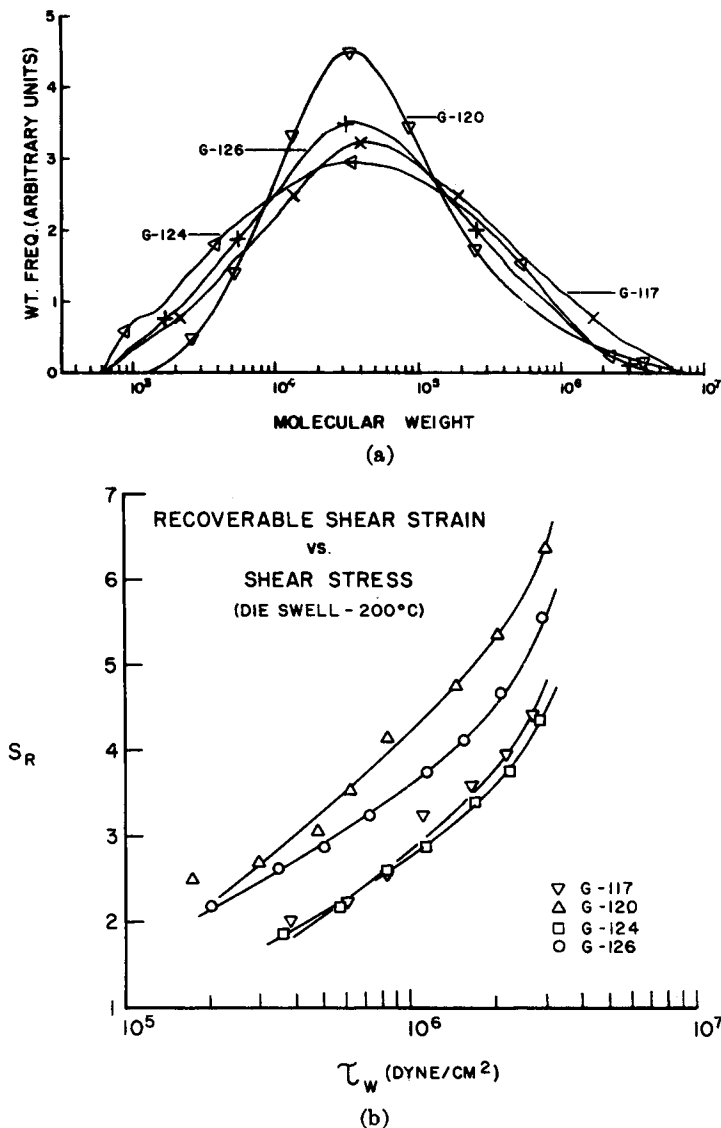
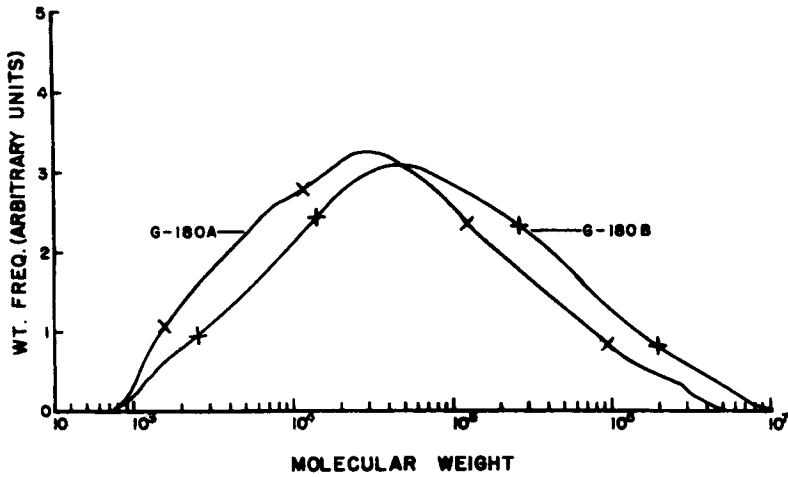


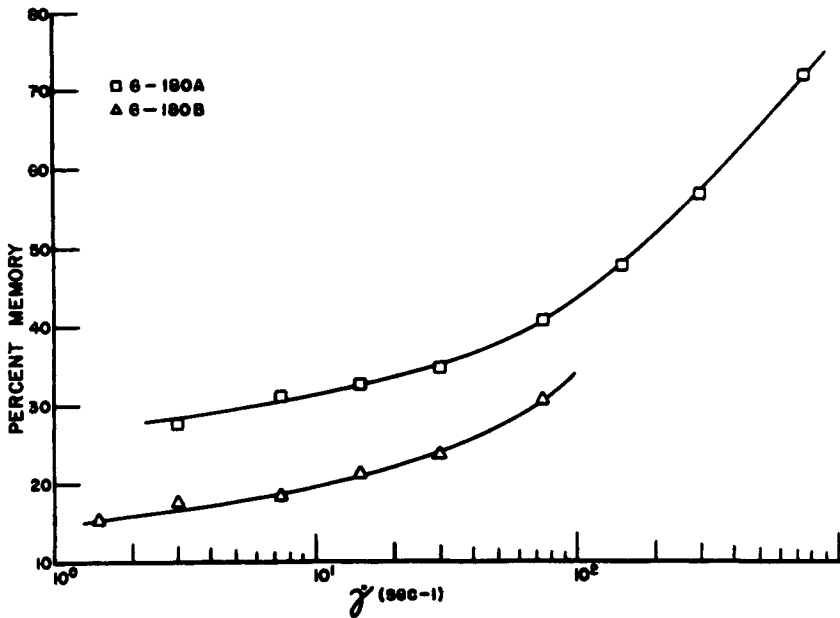
Fig. 8. (a) Comparison of MWD curves from GPC for (∇) G-120; (+) G-126; (\triangleleft) G-124; (X) G-117; and (b) recoverable shear strain vs. shear stress at 200°C (0.05 in. \times 2.0 in. \times 90° capillary) for (Δ) G-120; (O) G-126; (\square) G-124; (∇) G-117.

tion on extrudate memory is shown in Figure 7b where the narrow-distribution sample G-121 has a much higher memory level at all shear rates than samples G-122 and G-136 whose memory curves are essentially identical as expected from their similar MWD curves.

A similar comparison of four samples at a different constant modal value (ca. 35,000) is shown in Figure 8a (MWD curves) and Figure 8b (S_R -versus- τ_w curves). Again the essential feature appears to be that the elastic response decreases with broadening MWD. The almost identical recoverable shear strain curves of samples G-117 and G-124, which have similar distributions but are somewhat displaced one from the other in MW level, may suggest that actual



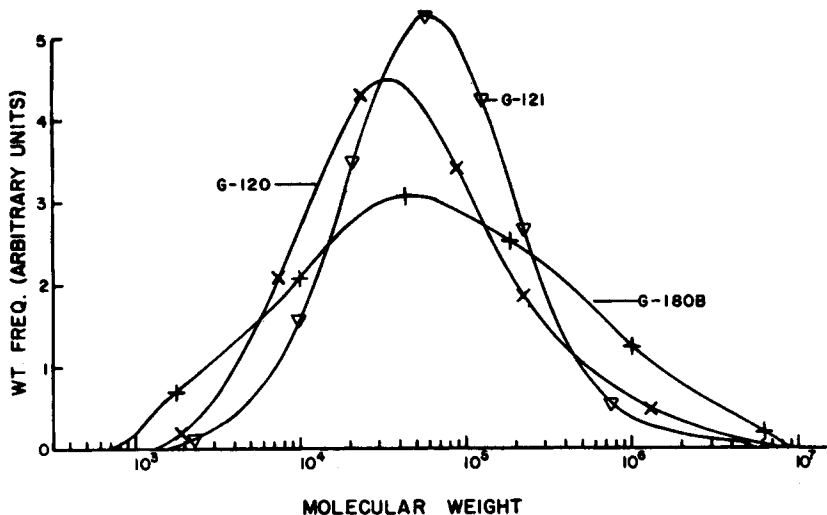
(a)



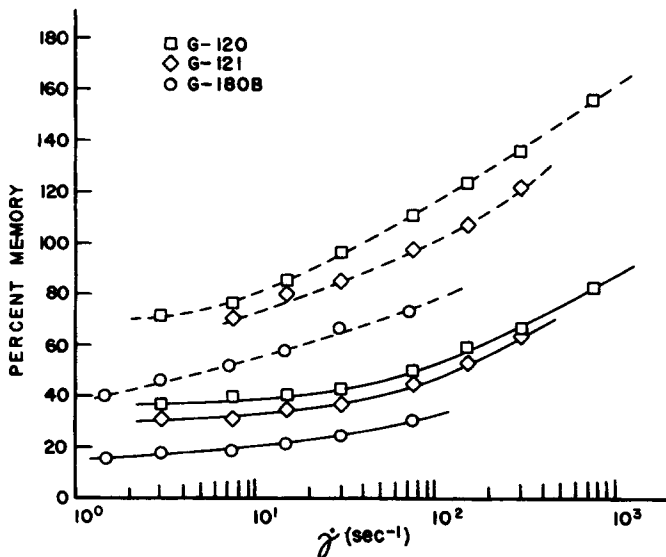
(b)

Fig. 9. (a) Comparison of MWD curves from GPC for (x) G-180A; (+) G-180B; and (b) per cent memory (unannealed) vs. shear rate at 200°C (0.05 in. × 2.0 in. × 90° capillary) for (□) G-180A; (Δ) G-180B.

breadth of distribution rather than high moment MW average is controlling. However, this suggestion is not very strongly supported by a comparison of two very broad-distribution samples, G-180A and G-180B, where one (G-180B) is displaced to significantly higher MW (\bar{M}_w/\bar{M}_n is also somewhat higher). Figures 9a and 9b show the comparative MWD and memory curves, respectively, for these samples indicating the higher memory at all shear rates for the lower MW (and narrower-MWD) sample.



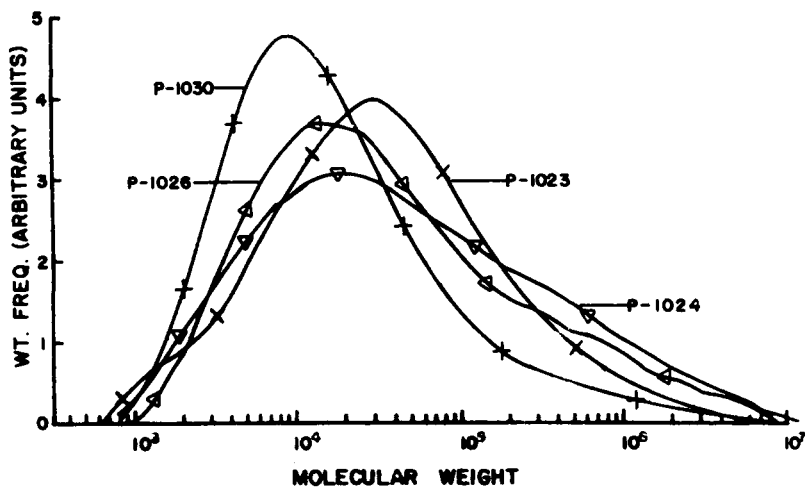
(a)



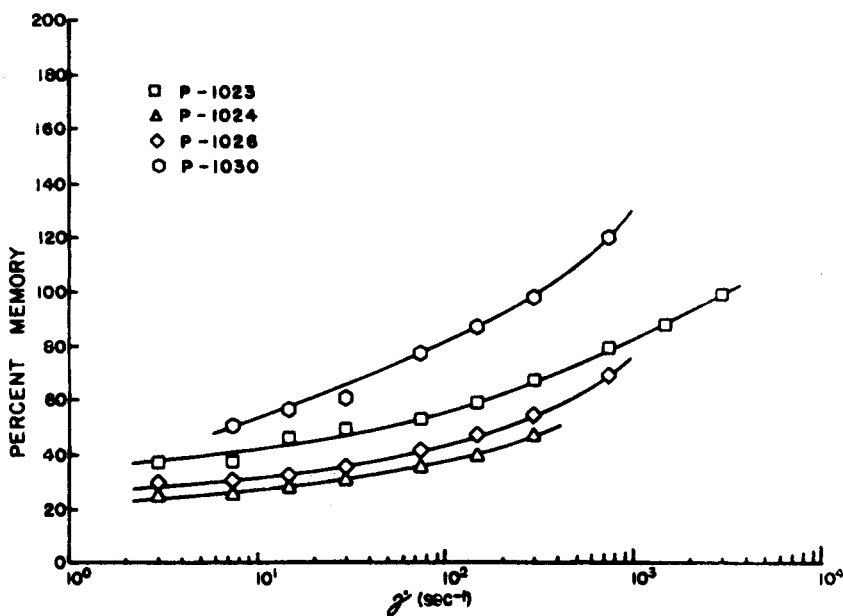
(b)

Fig. 10. (a) Comparison of MWD curves from GPC for (∇) G-121; (\times) G-120; (+) G-180B; and (b) per cent memory vs. shear rate at 200°C (0.05 in. \times 2.0 in. \times 90° capillary) for (\square) G-120; (\diamond) G-121; (\circ) G-180B; solid lines: unannealed memory; dashed lines: annealed memory.

Other comparisons of groups of these samples could be cited (e.g., compare G-120 and G-122) with the same qualitative results. In no case can it be said that an increase in memory is observed with increasing $(\bar{M}_z \bar{M}_{z+1} / \bar{M}_w)$. In one particular comparison shown in Figures 10a and 10b, an exception to the trends observed above may be seen. Here the order of broadening MWD is G-121, G-120, G-180B. However, the order of decreasing memory is G-120, G-121, G-180B. In other words, in this comparison, memory first rises with increasing high MW average or broadening MWD and then decreases for the very broadest-



(a)



(b)

Fig. 11. (a) Comparison of MWD curves from GPC for (+) P-1030; (x) P-1023; (<) P-1026; (v) P-1024; and (b) per cent memory (unannealed) vs. shear rate at 200°C (0.05 in. × 2.0 in. × 90° capillary) for (○) P-1030; (□) P-1023; (◇) P-1026; (Δ) P-1024.

MWD sample. It is perhaps significant that the two samples, G-121 and G-122, showing the more generally accepted trend, as opposed to the behavior generally encountered in this investigation, were the two narrowest-MWD samples studied and are considerably closer in breadth of distribution to samples for which published data are available than are the other samples studied here.

Finally, we examine the effect of MWD on memory for the third group of samples (P-samples), the shape of whose distributions differ from that of the

G-samples due to skewing toward the high MW end. Figure 11a compares the MWD curves of these four samples. The skewed shape (on a logarithmic MW scale) compared to the relatively symmetrical shape previously observed for the G-samples is apparent. For this set of samples, both the breadth of distribution (measured by \bar{M}_w/\bar{M}_n) and MW increase in the order P-1030, P-1023, P-1026, P-1024, which is precisely the order of decreasing memory, as illustrated in Figure 11b. Thus, the skewed distribution polymers show the same qualitative behavior as the more symmetrical distribution materials.

No theoretical or detailed mechanistic explanation of the above results is attempted at this time. One difficulty lies with the multiplicity of and generally correlated nature of the molecular parameters describing MW and MWD of broad and variously shaped MWD polymers. This difficulty is obviated, at least in a qualitative sense, by considering overall distribution curves rather than specific moments or combinations of moments. A second difficulty lies in the reliability, on an absolute basis, of the molecular characterization. This is never a simple problem and is particularly complex for broad-distribution polymers, and more particularly for crystalline polymers which must be characterized in solution at elevated temperatures. In this regard, the use of several independent forms of calibration combined with interlaboratory checks,³² such as have been employed with our GPC work, is important. Thus, the use of *p*-xylene at 105°C for the intrinsic viscosity measurements and of 1,2,4-trichlorobenzene at 135°C for the GPC analysis conforms to the requirement of thermodynamically "good" solvents to prevent possible erroneous measurements due to association or aggregation.³³⁻³⁵ Similarly, the calibration of the GPC using fractions, themselves characterized in several ways in different solvents at different temperatures,²⁴ and the check of that calibration against other well-characterized polymers by means of the universal calibration method²⁵⁻²⁸ may be expected to lead to a high degree of reliability and accuracy. Even so, the values of \bar{M}_z and \bar{M}_{z+1} must be considered only approximate at the very best. Considering the problems associated with molecular characterization of polyethylene, any correlation of melt rheological behavior with molecular structure where considerable care is not devoted to the molecular characterization must be considered suspect.

Turning to the rheological behavior, the agreement in die swell data between the undissolved sample F-101 and the dissolved and reprecipitated F-102A (substantiated in a number of other similarly performed tests, not reported here³⁶) is in sharp contrast to results on fractions reported by Schreiber and Bagley.³⁷ In their work they reported very substantial reduction in die swell as a consequence of dissolution and reprecipitation, presumably because of chain disentanglement during the dissolution process. However, in their work the dried reprecipitated polymer was never subjected to a thermal history permitting reentanglement prior to rheological testing, whereas in the current work all samples were, indeed, reheated during compression molding and given the opportunity both at that time and during the thermal equilibration period prior to extrusion through the test capillary to achieve equilibrium reentanglement. Thus, the results of Schreiber and Bagley may be ascribed to an unentangled system while the current results represent the response of the entangled polymer state.

It is clear that summing (with any weighting method) the noninteracting contributions of each molecular species will not predict even the direction of variation of melt elastic deformability observed in this investigation. Thus,

both the number and complexity of entanglements in which the individual molecules are involved may have to be taken into account. The contrast between the increasing (or constant) recoverable shear strain or elastic compliance with increasing MW observed for narrow-MWD materials and the current results for very broad-distribution polymers, coupled with the somewhat ambiguous behavior of intermediate-MWD materials studied here (F-107, G-121), may indicate that in such a continuum of species' sizes (as opposed to blends of distinctly separate species) the very large molecules may act to inhibit the elastic deformation during shear of the intermediate sized species (perhaps by multiple entanglement coupling) in the time period of the application of stress. This suggests that there may, in fact, be a maximum in the relationship between memory (elastic deformability) and MW as MWD broadens. Thus, in a narrow-distribution material all species support the stress to some degree by elastic deformation; as the distribution broadens, the larger species first tend to attain greater overall elastic deformation in the shear field; but, with continuing broadening of the distribution, the very high MW species tend to become so involved in entanglements that their contribution to overall elastic deformation decreases and they tend as well to reduce the ability of the somewhat lower MW species with which they are entangled to react to the deforming shear stress in the experimental time available.

Thus, while the carefully designed experiments described herein are empirical in nature, they reveal an unexpected, but important, form of die swell dependence on the molecular weight distribution of HDPE which requires explication if we are to be able to predict the melt properties of polymers from molecular considerations.

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