

## Some Studies on the Swelling Behavior of Polyethylene

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### Synopsis

When polymers are extruded from a capillary, the amount of extrudate swelling is generally found to be a function of shear rate and capillary dimensions. Experiments with polyethylene now show that when shear rate is replaced by an average transit time in the capillary, postextrusion swell becomes a function of transit time only. Plots of swell versus transit time are independent of the applied stress and reduce to a single line for capillaries of different dimensions. The swell was found to be dependent upon the average molecular weight and the molecular weight distribution. Little correlation, however, was found with the amount of high molecular weight fractions.

### INTRODUCTION

Generally, studies on the elastic behavior of polymer melts have been carried out in expensive rotational viscometers,<sup>1,2</sup> involving large deformations and recovery periods of seconds to several hours. The time scale of the deformation and recovery and the absolute magnitude of the deformation are important factors in determining the elastic properties of viscoelastic melts. Often, these factors vary widely in different tests, and so results cannot be compared.

Another experimental approach is through capillary rheometry.<sup>3-5</sup> Bagley et al.<sup>6</sup> found that the swell properties of polyethylene decreased with increasing capillary length, at a constant shear stress, although the viscosity remained constant. A recent publication<sup>7</sup> showed that nonlinear plots of pressure versus capillary length-to-radius ratio, at constant shear rate could be accounted for by the elastic behavior of the melt during transit through the die. This communication discusses some studies on the swell behavior of polyethylene in different dies in terms of the time of passage through the die and the polymer's molecular structure.

### THEORY

In the extrusion of polymers through a capillary, the diameter of the extrudate is often found to be larger than the diameter of the capillary. This is the result of recovery of the elastic energy stored within the melt because of distortion or orientation of the molecules by the shearing stresses.

If Hooke's law in shear is assumed to be obeyed,<sup>7,8</sup> then the shear stress at the wall,  $\tau$ , and the elastic shear strain,  $\lambda_e$ , are related to the degree of swelling,  $\alpha$ , by eqs. (1) to (4):

$$\lambda_e = J_e \cdot \tau \quad (1)$$

$$J_e = \frac{2}{5} \frac{M}{\rho RT} \quad (2)$$

$$\alpha = D_e/D_c \quad (3)$$

$$\lambda_e = \alpha - 1/\alpha \quad (4)$$

where  $J_e$  is the elastic compliance,  $M$  is the molecular weight of the polymer,  $D_e$  is the diameter of the extrudate, and  $D_c$  is the diameter of the capillary, and  $\rho$ ,  $R$ , and  $T$  are, respectively, melt density, gas constant, and melt temperature. If  $Q$  (in cubic centimeters per sec) is the output rate through a capillary of diameter  $D_c$  and length  $L$  then an average transit or residence time  $t_a$  may be defined by:

$$t_a = \pi D_c^2 \cdot L / 4Q. \quad (5)$$

If the polymer obeys the power law,

$$\tau = K \left[ \frac{32Q}{D_c^2} \right]^n, \quad (6)$$

then it can be shown that substituting eq. (5) into eq. (6) and combining with eqs. (1), (2), and (4) for a polymer of constant molecular weight, the logarithmic plot of swell versus transit time will have a slope  $-n$  and will be linear only if the polymer shows little non-Newtonian behavior. Further, swell measurements from different capillaries, when expressed in terms of the average transit time through the capillary, will reduce to a single line.

Again, a combination of eqs. (1) through (6) shows that the swelling of the polymer at either constant shear stress or at constant shear rate will be directly proportional to its molecular weight. Ferry<sup>9</sup> has given an alternative equation to eq. (2) involving  $(z + 1)$ -average,  $z$ -average and weight-average molecular weights:

$$\bar{M} = \frac{N_i \cdot M_i^{n+1}}{N_i \cdot M_i^n}$$

where, when  $n = 0$ ,  $\bar{M}$  is the number-average  $\bar{M}_n$ ; when  $n = 1$ ,  $\bar{M}$  is the weight-average  $\bar{M}_w$ ; when  $n = 2$ ,  $\bar{M}$  is the  $z$ -average  $\bar{M}_z$ ; and when  $n = 3$ ,  $\bar{M}$  is the  $(z + 1)$ -average  $\bar{M}_{z+1}$ ; and eq. (2) becomes

$$J = \frac{2 \cdot \bar{M}_{z+1} \cdot \bar{M}_z}{5 \cdot \bar{M}_w \cdot RT} \quad (7)$$

Equation (7) would predict that a polymer with a broad distribution would have greater extrudate expansion than one with a narrower distribution of similar weight-average molecular weight.

## EXPERIMENTAL

An Instron rheometer,<sup>10</sup> a melt indexer,<sup>11</sup> and a Babenderextruder<sup>12</sup> were used to compare the swell properties of polymers at different transit times and in different capillaries. Samples of the extrudate were carefully taken to minimize drawdown effect, and the diameters of the slowly cooled extrudates were measured approximately 0.25 in. from the initially extruded end. The ratio of extrudate diameter to the capillary diameter gave a measure of the swell. Strictly speaking, either the diameter of the molten extrudate or the diameter of the annealed extrudate should have been measured.<sup>13</sup> The former was difficult experimentally, and measurement of the latter showed changes of from 0.5 to 1.0% when the extrudate was annealed for up to one week in an air oven at 100°C. This was considered to be within experimental reproducibility. One-minute cuts of output rate were also taken in order to determine the corresponding transit times, eq. (5). Five grades of commercially available polyethylenes were used for comparing the swell properties of the polymer in various capillaries (Table I).

TABLE I

Sample no.	Resin type
C-6	0.95 g/cc density ethylene-butene copolymer, 0.21 dg./min melt index
D-4	0.96 g/cc density ethylene homopolymer, 0.73 dg./min melt index
D-5	0.96 g/cc density ethylene, low-swell homopolymer, 0.82 dg./min melt index
K-1	Ziegler-type commercial ethylene homopolymer, 0.82 dg./min melt index
L-1	Phillips-type ethylene-butene copolymer, 0.26 dg./min melt index

For the determination of swell versus molecular structure, swell measurements for 18 samples of commercial and experimental polyethylenes were determined on a melt indexer having a 0.825-in. diameter, 0.316-in.-long capillary. The melt indexer barrel was charged with 7 g of the sample, and after allowing 10 min to equilibrate, swell and output measurements were taken using loads of 2 to 20 kg. The polymer characteristics as determined by gel permeation chromatography are listed in Table II. The standard deviations were  $\pm 5\%$  for  $\bar{M}_n$ ,  $\pm 2.5\%$  for  $\bar{M}_w$ ,  $\pm 2.2\%$   $\bar{M}_z$ , and  $\pm 2.5\%$  for  $\bar{M}_{z+1}$ .

## RESULTS

## Swell Versus Transit Time

It has been shown previously that the swelling rate of a polymer increases as the rate of shear (throughput) increases or as the capillary length

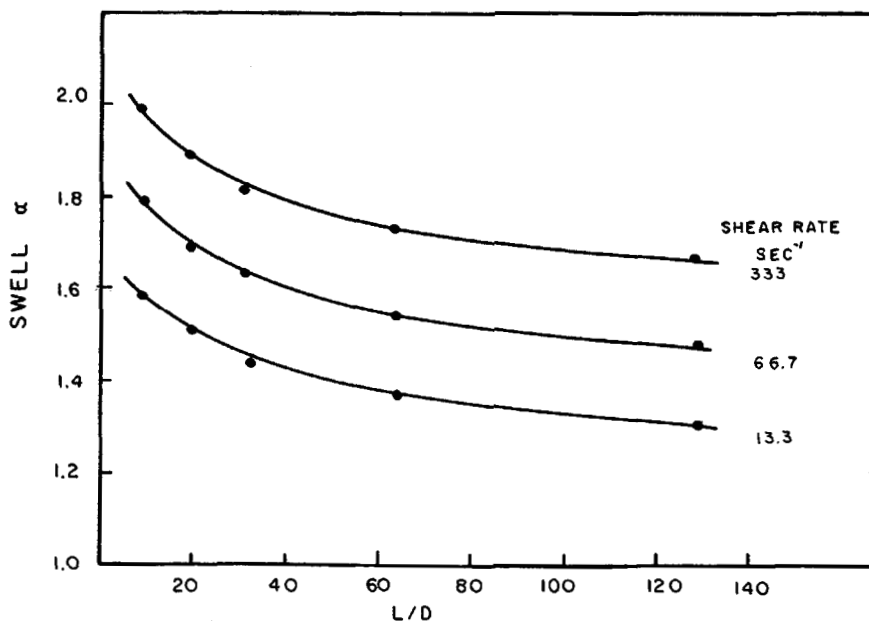


Fig. 1. Effect of capillary dimensions on extrudate swell at constant shear rates measured on Instron rheometer. Sample D-4, melt temperature 200°C.

decreases.<sup>5-7</sup> This is again illustrated in the present results (Fig. 1). When the data from several capillaries and from different tests were combined and the results were expressed in terms of the average transit time, typical Figures 2, 3, and 4 were obtained. Although some scatter is present, it is clear that the prediction of the theory is essentially observed. That is, the swelling property of a given polymer depends on the transit

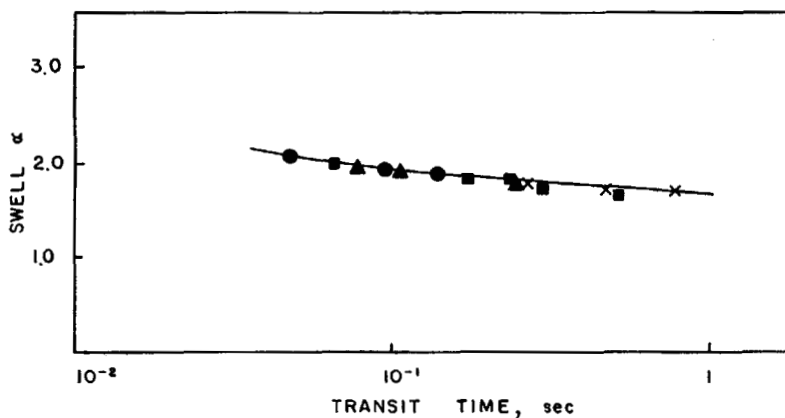


Fig. 2. Effect of transit time on swelling of sample D-5 measured at 200°C melt temperature on Brabender extruder: (X) capillary  $L/D = 15/1$ ; (■) capillary  $L/D = 10/1$ ; (▲) capillary  $L/D = 5/1$ ; (●) capillary  $L/D = 3/1$ .

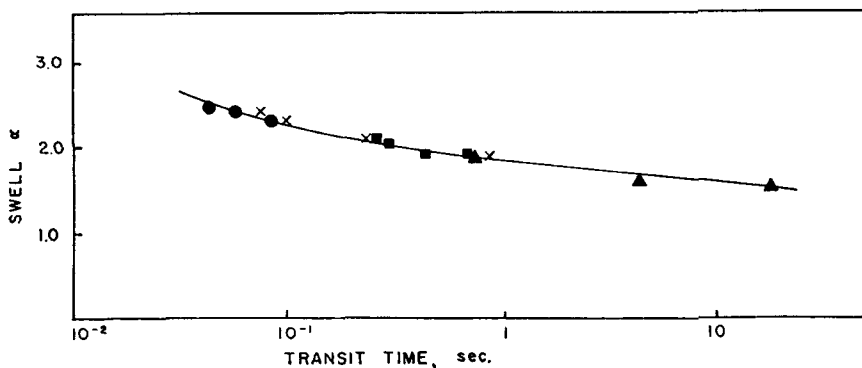


Fig. 3. Comparison of swell versus transit time as measured on Brabender and melt indexer. Sample C-6, melt temperature 190°C. Brabender capillary: (●)  $L/D = 15/1$ ; (×)  $L/D = 5/1$ ; (■)  $L/D = 3/1$ . (▲) Melt indexer.

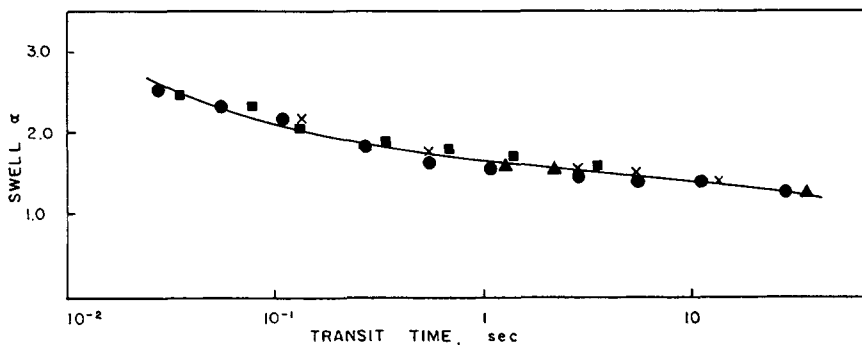


Fig. 4. Comparison of swell versus transit time as measured on Instron rheometer and melt indexer. Sample L-1, melt temperature 200°C. Rheometer capillary: (●)  $L/D = 20/1$ ; (×)  $L/D = 10/1$ ; (■)  $L/D = 2.5/1$ . (▲) Melt indexer.

time in the capillary. Several explanations have been proposed to explain postextrusion swelling,<sup>6,14-18</sup> but the literature is not clear in establishing a relationship between swelling behavior and melt temperature. Miller<sup>18</sup> reported that swelling increased with decreasing temperature, while Mills et al.<sup>19</sup> have reported the reverse. In the present work, it was found that swell was independent of temperature over the range 170° to 200°C (Figs. 5 and 6). This result agrees with that of Metzger and Matlack<sup>5</sup> for high-density polyethylene over the temperature range of 180° to 200°C.

Although the simple theory outlined above predicts, and has been confirmed by experiment, that swell is inversely proportional to the transit time, McIntosh<sup>14</sup> has developed a theory describing the extent of swelling of a viscoelastic liquid and has shown that at high shear stresses the swelling passed through a maximum. In the present experiments, the point of melt fracture was reached before any point of maximum swelling was detected.

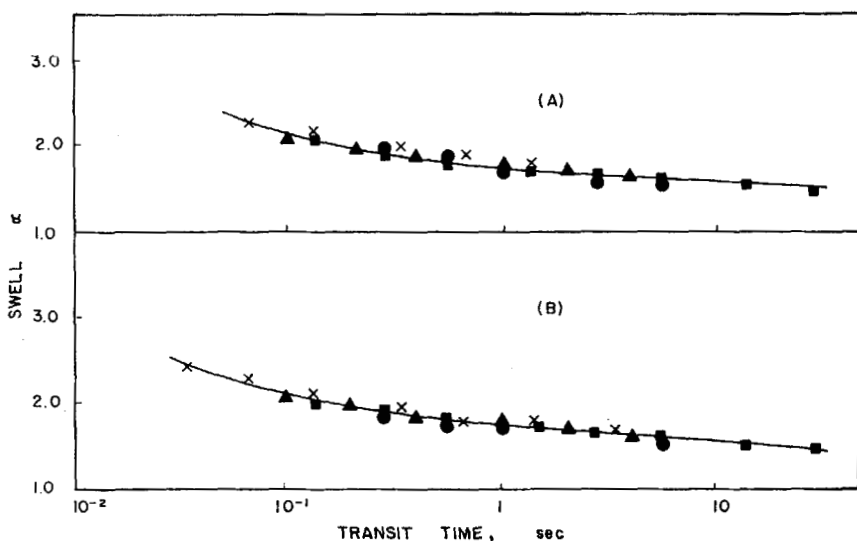


Fig. 5. Comparison of swell versus transit time as measured on Instron rheometer. Sample C-6, melt temperatures 170°C (A) and 200°C (B): ( $\times$ )  $L/D = 2.5/1$ ; ( $\blacktriangle$ )  $L/D = 7.5/1$ ; ( $\blacksquare$ )  $L/D = 10/1$ ; ( $\bullet$ )  $L/D = 20/1$ .

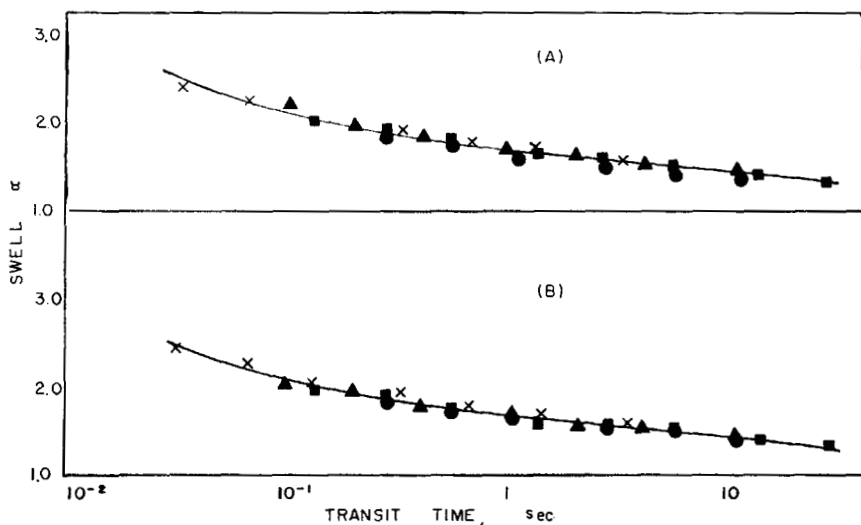


Fig. 6. Comparison of swell versus transit time as measured on Instron rheometer. Sample L-1, melt temperature 170°C (A) and 200°C (B). ( $\times$ )  $L/D = 2.5/1$ ; ( $\blacktriangle$ )  $L/D = 7.5/1$ ; ( $\blacksquare$ )  $L/D = 10/1$ ; ( $\bullet$ )  $L/D = 20/1$ .

### Swell Versus Molecular Weight

The swell properties of a number of characterized samples, (Table II) were determined for transit times of 10 sec and 0.2 sec corresponding, respectively, to shear rates of  $3.06 \text{ sec}^{-1}$  and  $153 \text{ sec}^{-1}$ . Figure 7 shows plots

TABLE II  
GPC Data<sup>a</sup>

Sample no.	$I_2$ , °C/min	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_z$	$\bar{M}_{z+1}$
1	5.74	90	16	650	1600
2	5.41	100	17	730	1700
3	4.66	135	7	980	1800
4	4.88	100	13	460	1000
5	6.43	130	7	940	1700
6	5.24	116	11	900	1900
7	6.25	124	13	960	1900
8	7.00	123	10	1000	2000
9	6.43	88	15	620	1600
10	6.44	97	11	730	1700
11	6.57	89	17	580	1600
12	6.33	86	12	550	1400
13	6.56	79	17	400	1100
14	7.35	84	21	580	1700
15	5.63	158	5	1600	2700
16	3.72	126	6	1100	2100
17	3.45	111	6	1200	2600
18	5.72	129	3	1200	2300

<sup>a</sup> Molecular weight values are in thousands.

of swell versus weight-average molecular weight,  $\bar{M}_w$ . Although some scatter in the point is evident, the data show that swelling increases linearly with increasing molecular weight. A similar trend is also seen in Figure 8 when swell is plotted against the molecular weight distribution,  $\bar{M}_w/\bar{M}_n$ . Sample numbers 2, 15, and 18, three ethylene-butene copolymers, show the greatest deviation from the linear plots and could possibly form another family of curves. Further data on the effects of copolymerization on the swell behavior is not available at the present time. McCord and Maxwell's results<sup>1</sup> indicated that increasing the molecular weight beyond a certain point, approximately 400,000, does not appreciably increase the swell properties. The results also show that not only do molecular weight and molecular weight distributions affect the amount of recovery but also the time of application of the stress. This is discussed below in terms of Busse's "cluster theory."<sup>20</sup>

In terms of what physically happens to the polymer, it can be seen that just prior to extrusion the polymer is in a molten and relaxed form. On application of a load or stress, it is compressed and extruded through the capillary. If the capillary length is short, or the rate of extrusion high, the polymer chains as a whole do not have sufficient time to respond to the compressive forces in the capillary. This results in deformation occurring primarily on a small local scale and leaves the bulk of the network structure undisturbed. For two polymers having similar weight-average molecular weights, the polymer with the greatest  $\bar{M}_n$  value will respond the quickest to the compressive forces and will, therefore, have the least extrudate

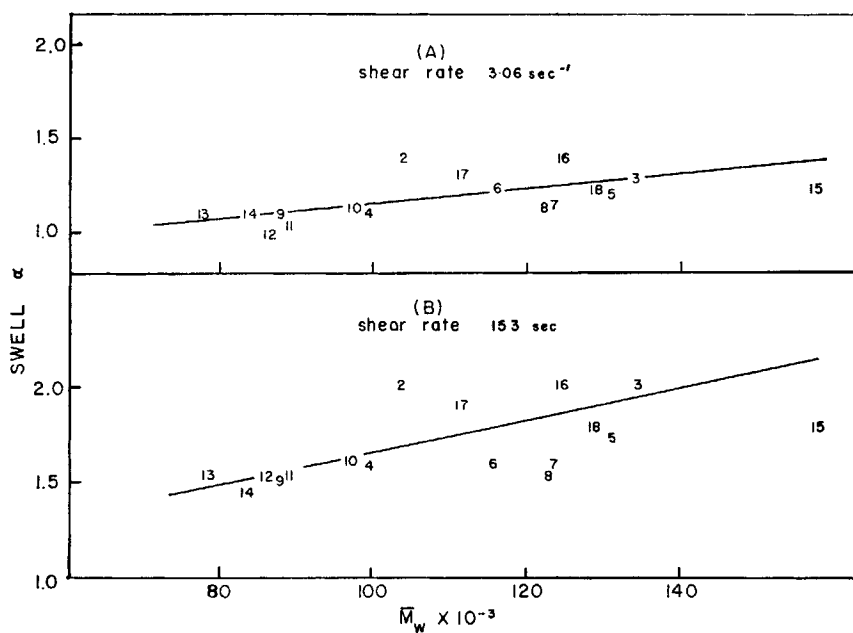


Fig. 7. Effect of weight-average molecular weight on swelling behavior.

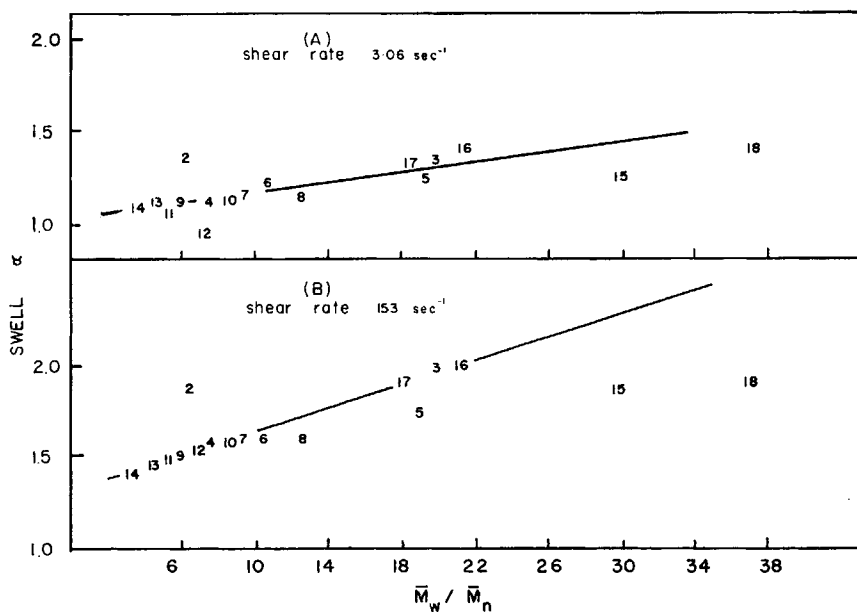


Fig. 8. Effect of molecular weight distribution on swelling behavior.



swelling. That is, at short transit times in the capillary, the swell is controlled largely by the low molecular weight fraction of the polymer. Similar findings have been indicated by Chartoff and Maxwell<sup>21</sup> using an orthogonal rheometer.

As the transit time in the capillary is increased, either by decreasing the rate of extrusion or by increasing the capillary length, the proportion of the polymer network that can respond to the application of stress is increased. The high molecular weight fraction of the polymer would then become of greater importance. Equation (7) predicts that the molecular weight of the highest fractions should control the extrudate swell. Figure 9, however,

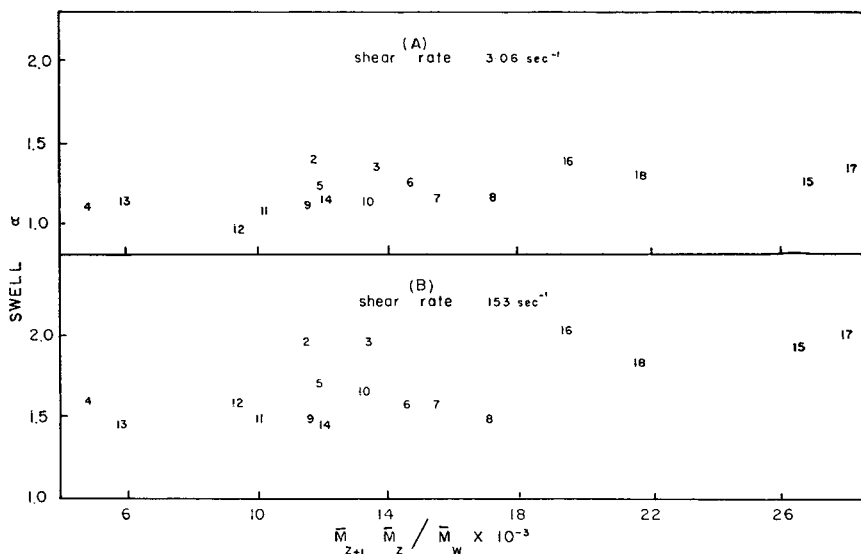


Fig. 9. Effect of high molecular "tail," as measured by  $(\bar{M}_{z+1} \cdot \bar{M}_z) / \bar{M}_w$ , on swelling behavior.

shows little correlation between the high molecular weight fractions, as measured by the  $(\bar{M}_{z+1} \cdot \bar{M}_z) / \bar{M}_w$  ratio, and extrudate swell. Possibly, the time scale of the experiments was too short to allow the polymer chains as a whole to respond to the applied stress. The net result is that swell appears to be governed by the low molecular weight fractions and the weight-average molecular weight of the polymer.

## DISCUSSION

Busse<sup>20,22</sup> has discussed the flow and elasticity of molten polymers in terms of Brownian motion of "pop-it beads," representing a polyethylene chain magnified 25 millionfold. Although Busse did not present any mathematical analysis, his "mental experiment" is useful for discussing the current results.

If it is imagined that several chains are present in a cubic array, the coils can overlap and cause entanglements randomly distributed throughout the volume. Those entanglements involving only slight overlaps of the chains will cause relatively little resistance to the motion of the chains past each other and will entail short relaxation times. As the number and length of the chains are increased, large overlaps and greater entanglements can occur. These would require coordinated motion of long sections of the chains to slip molecules through the entanglements, so very long relaxation times and large resistances to motion could develop. When the array of molecules is subjected to a small shear displacement, there will be a small deformation of the polymer which may be relieved by the Brownian motion of a small number of atoms. As the shear is continued at a constant rate, more entanglements can be formed as the interpenetrating molecules with different velocities sweep past each other. If the normal segmental Brownian motion of the chain segments cannot disentangle the intersecting chains in some small fraction of a second, the entanglement points on a given molecule may be pulled further apart by the imposed shear. This can distort the random coils between the entanglement points sufficiently to produce large elastic displacements and large tension differences in the chains before the slippage rate can keep up with the imposed shear rate. This gives the large recoverable elasticity observed in capillary flow experiments.

A consequence of Busse's mental picture that the slippage at an entanglement depends upon the amount of random coil deformation is that the percentage recovery (swell) for a particular polymer is nearly independent of the load for a given time of application of the load. This has been seen (Figs. 2, 3, 4, 5, 6) where the swell obtained from different capillaries is the same for any given transit time in the capillary.

## CONCLUSIONS

Theoretical predictions, based on well-known theories of polymer flow, that extrudate swell of a given polymer from a capillary was dependent upon the time of application of a load and independent of the magnitude of the load were confirmed experimentally.

The influence of the low molecular weight fractions was also illustrated, although the role of the high molecular weight tail was less obvious.

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