Time-Dependent Capillary Flow of Polystyrene

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Synopsis

The nonsteady flow behavior of a characterized commercial polystyrene has been examined in a compressed-nitrogen-gas piston viscometer. Nonsteady flow data were erratic with virgin polymer at 173.9°C. Pretreatment of the polystyrene by subjecting the melt to a higher temperature, with or without shear, changed the nature of the time-dependent flow to that which is generally characteristic of polymers in experiments of this type. The pretreatment had no significant effect on the equilibrium flow curve at the same temperature nor on the molecular weight of the polystyrene. The results are interpreted in terms of changes in the size or nature of supermolecular flow units.

INTRODUCTION

In capillary extrusion of thermoplastic melts time-dependent changes in viscosity may be observed, although the experimental conditions and polymer are both apparently invariant. The subject has been reviewed recently, with particular reference to results from viscometers operated by deadweight[1] and compressed-gas pistons.[2] The curve in Figure 1 is typical of the relation between apparent shear rate and time after application of a constant extrusion pressure in a gas-operated capillary rheometer such as the one used in the present work.[3] The shear rate–time curve exhibits a minimum at a steady apparent shear stress. In viscometers that operate at a constant shear rate, the corresponding variations with time would be maxima in the shear stress or extrusion pressure. Such observations have been reported for polychloroprene and polyisoprene compounds,[4] polystyrene,[5] poly(vinyl chloride) and polyethylene[6] and, very recently, solutions of polystyrene and poly(methyl methacrylate) in chlorinated diphenyl.[7] Further investigation is required, however, because of inconsistencies in the reported magnitudes of such effects and in their interpretation.[1,2]

In the present study the nonsteady flow of a characterized polystyrene is examined with a constant-pressure (gas piston) capillary viscometer. The results indicate that time-dependent viscosity of a polymer melt may be a function of its heat and shear history in addition to the already established effects of polymer molecular structure and experimental conditions. Nonsteady flow of polystyrene has been studied at constant apparent rate of shear by Ballman[8] and by Komuro and his co-workers.[5]
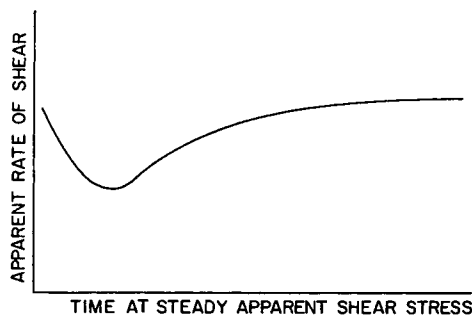
Fig. 1. Time variation of apparent rate of shear in constant-pressure capillary extrusion.[1,2]

EXPERIMENTAL

The polystyrene, donated by Kayson Plastics and Chemicals Limited, was commercial, bulk-polymerized grade, with the characteristics listed in Table I.

Molecular weight averages were determined from gel permeation chromatography elution curves. A Waters Associates model 200 chromatograph was used, with four stainless-steel columns, each with length 4 ft and inside diameter 0.375 in., connected in series. Column packings were rigid polystyrene gel of stated pore sizes 3×10^6, 10^5, 10^4, and 10^3 Å. The eluant was tetrahydrofuran. Molecular weight averages were computed from elution curves by Tung's Hermite polynomial method.[10]

The polystyrene was stabilized against thermal degradation by tumbling granules for about 16 hr with 0.2 or 0.5% (w/w) of commercial 2,6-di-*tert*-butyl-4-methyl phenol antioxidant. Evidence presented below showed that the lower antioxidant concentration prevented significant change in the molecular weight distribution of the polymer. The stabilizer had no detectable effect on the polymer flow curve at the concentrations used.

Melt flow measurements were made with a compressed-nitrogen-operated capillary rheometer[11] with barrel diameter 1.58 cm and length 20.4 cm. Melt temperature can be controlled to ±0.2°C. Capillary orifices were drilled steel disks with flat (180° included angle) entries. A 15-min waiting

TABLE I
Polystyrene Molecular Weights

Sample	M_n	M_w	M_z	Std. devn.[a]
As received	61 900	312 500	685 500	125 000
Extruded[b]	60 800	285 150	628 000	117 000

[a] Standard deviation of number distribution, $(M_w M_n - M_n^2)^{0.5}$.[9]

[b] This material was extruded at 216°C through a capillary of radius 0.036 cm and length 1.270 cm with a driving pressure of 1900 psi of compressed nitrogen. The extrudate was used for a flow curve measurement at 173.9°C through an orifice of radius 0.035 cm and length 0.201 cm. The extrudate from the flow curve determination was sampled for molecular weight measurement.

period, after the polymer was loaded and tamped in the reservoir, was sufficient for temperature equilibration. Polystyrene wets steel well, so that a loose-fitting steel ball-bearing riding above the polymer melt effectively prevented channeling of the compressed nitrogen. Flow curves were derived from raw data consisting of weights of timed extrudates at stipulated driving pressures, orifice dimensions, and reservoir temperatures. Shear rates were computed from the weights by using published specific volume–temperature data.[12]

All flow curves were measured under standard conditions and were used only to compare samples of the same polymer having different heat histories. It would, therefore, have added nothing to correct apparent shear rate–shear stress data for melt compressibility or elastic end effects. For the same reason the Mooney-Rabinowitsch relation[13] to convert apparent to wall shear rates was not applied. Errors due to variable pressure losses in the reservoir were avoided through use of a standard loading for each flow curve measurement. Kinetic energy corrections were negligible, and it seemed reasonable to assume that shear heating effects would not differ significantly between samples.

Nonsteady flow rates were measured at a constant extrusion pressure and recorded as weights of extrudate per unit time. These measurements are not instantaneous. The flow rate plotted against a particular time represents the average rate in the interval between the recorded and preceding data points. Zero on the time scale corresponds to application of extrusion pressure.

RESULTS

Thermal Stability

Flow behavior in the unsteady state was measured with samples subjected to various prior heat treatments. It was therefore important to determine whether this variable heat history had caused any significant change in the molecular weight distribution of the polymer. Both the equilibrium and time-dependent flow properties of polymer melts can be severely altered by thermally induced changes in molecular structure and intermolecular aggregation.[14,15] The results of gel permeation chromatography and flow curve measurements showed that such changes are not significant in the nonsteady flow reported below.

GPC molecular weight averages are recorded in Table I for virgin polymer and for a sample which had been subjected to as severe heat and shear conditions as any used in the present study. The slight changes listed are unlikely to be significant in terms of the precision of the analytical method and are opposite in direction to those which could most logically account for the variations in nonsteady flow behavior which are noted below.

Flow curves were measured at the same temperature (173.9°C) and with the same orifice (length 0.201 cm, radius 0.035 cm) as were used in the nonsteady flow experiments. The data obtained at shear stresses between 0.6
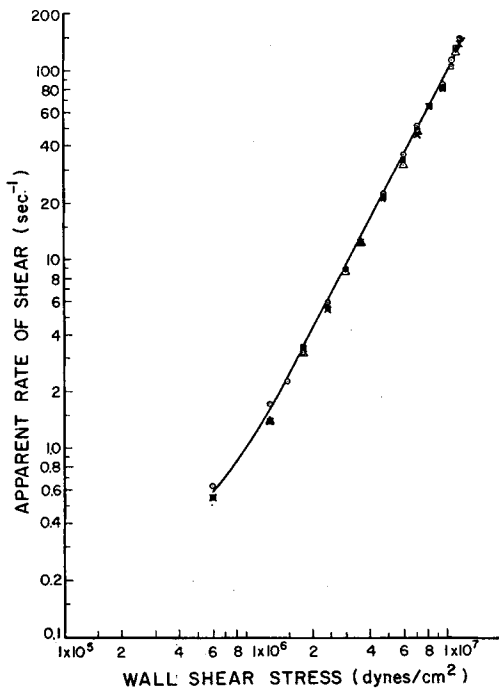
Fig. 2. Flow curves of samples with varying heat histories. Temperature 173.9°C. Orifice radius 0.035 cm, length 0.201 cm. Pretreatment (corresponding nonsteady flow rate run given in parentheses): (O) nil (1–4); (×) extruded at 216°C through above orifice at 6×10^6 dyn/cm² shear stress after 15 min dwell at 216°C (6–9); (□) 15 min dwell at 216°C, no extrusion (10); (△) as (×) except that orifice had radius 0.036 cm and length 1.270 cm (see footnote b Table I); (s) as (×) except that pretreat temperature was 250°C.

$\times$ 10^6 and 12×10^6 dyn/cm² are plotted in Figure 2 for samples representative of the range of heat histories used in subsequent time-dependent flow measurements. All experimental points can be represented by a single curve within the precision of the measurement technique. The greatest discrepancy at any shear stress is about 6% of the lowest corresponding apparent shear rate. These data support the conclusion that polymer molecular weight was essentially invariant.

The flow curve in Figure 2 is almost completely linear in the double logarithmic plot, with only a slight curvature away from the shear stress axis at apparent rates of shear less than 1 sec^{-1}. Stratton[16] measured flow curves of narrow-distribution polystyrenes and found pronounced deviations in this shear rate range for a polymer with approximately the same M_w as that used in the present work. The most likely reason for this difference between the two cases is the broader molecular weight distribution of the polystyrene used in our experiments. Newtonian behavior persists to higher shear rates as the distribution is narrowed about the mean molecular weight of the sample.[17,18]

Time-Dependent Flow

Nonsteady flow measurements were made at an extrusion pressure of 200 psi, corresponding to a wall shear stress of 1.20×10^6 dyn/cm² in the orifice used. This was slightly less than the shear stress (1.50×10^6 dyn/cm²) at which extrudate distortion occurred with this polymer. It was thus convenient to observe any changes in extrudate diameter or smoothness as the extrusion proceeded. Preliminary experiments at this shear stress showed that a melt temperature near 175°C was required to provide a flow rate sufficient to permit sampling the extrudate at 2 min intervals. At lower temperatures 5 min extrudate cuts were needed to obtain sufficient sample for accurate weighings. Time effects averaged over this interval were obscure.

Four replicate flow rate–time measurements were made with virgin polymer at 173.9°C with the same flat-entry capillary (radius 0.035 cm, length/radius 5.76). The results, shown in Figure 3, were erratic. Flow rates differed between experiments by more than 20%, which is well beyond the limits of precision of the technique. There was also little evidence of the characteristic output–time relation or smooth progression of flow rates depicted in Figure 1 and generally (although not invariably) observed in this type of measurement.

The data from these four experiments appear to fall into two groups, the higher flow rate pair (runs 1 and 3) exhibiting the greatest variability. All extrudates were smooth at the start of flow but developed a very slight distortion or twisting as the extrusion proceeded. The arrows in Figure 3 mark the onset of this mild distortion, which possibly is due to intermittent melt fracture.[19] The flow rates at the first sign of distortion were about 140×10^{-4} g/min for the higher flow experiments and 114×10^{-4} g/min for the lower flow rate pair. Shear stresses were identical in all four cases. All experiments were started with a standard loading of polystyrene in the viscometer reservoir (17.2 cm above the orifice, equal to 20.7 g of polymer).
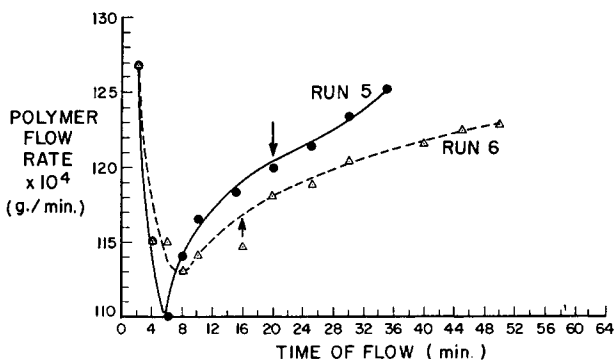

Fig. 3. Flow rate–time relation for virgin polystyrene. Temperature 173.9°C. Orifice radius 0.035 cm, length 0.201 cm. Polymer loading 17.2 cm above orifice.

The amount extruded during an entire experiment was of the order of 0.6 g, so that reservoir drainage effects, which can, conceivably, result in progressively increasing shear stresses at the orifice wall were not significant. It was unlikely that the erratic behavior noted was due to inadequate temperature equilibration in the viscometer, since flow curve measurements were precise (Fig. 2) at the same temperature and with the same preheat times. There was thus no experimental variable to account for the data represented in Figure 3.

Thermal History of the Melt

A sample of polystyrene was allowed to stand in the viscometer reservoir for 5 min at 216°C and was then extruded through the standard orifice used in all the preceding experiments at 6×10^6 dyn/cm^2 wall shear stress. A similar sample was prepared, except that the preheat time at 216°C was 15 min. The extrudates from these operations were used for flow rate–time measurements at 173.9°C under conditions identical with those described above for runs 1–4. The data from the latter experiments are plotted in Figure 4, where runs 5 and 6 correspond to samples with respective dwell times of 5 and 15 min at 216°C. The two flow rate–time curves do not coincide, but each is much less erratic than those observed with
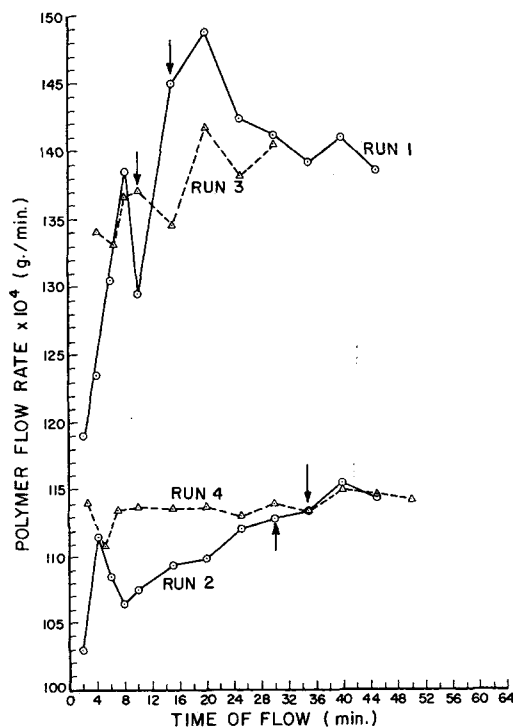

Fig. 4. Flow rate–time relation for pretreated polystyrene. Temperature 173.9°C. Orifice radius 0.035 cm, length 0.201 cm. Polymer loading 5.4 cm above orifice.

virgin polymer at the same temperature. The shapes of the curves re-
semble those generally found in time–flow rate experiments with other poly-
mers and compressed gas or deadweight-driven extrusion rheometers (Fig.
1). The range of extrusion rates is approximately that for the more viscous
pair of virgin polymer runs (Fig. 3), but the initial loading of polystyrene
was 5.4 cm above the orifice for runs 5 and 6, compared with 17.2 cm for
runs 1–4. Any influence of this difference should be toward higher flow
rates for runs 5 and 6, because of lower pressure losses in the reservoir.
Although pretreatment at 216°C had a significant effect on subsequent non-
steady flow of the polystyrene at 173.9°C, there was no corresponding effect
on the equilibrium flow curve at the latter temperature (Fig. 2).

Reservoir Drainage Effects

The standard pretreatment for the next series of experiments was the
same as that used for run 6 (see above). The effect of initial height of
polymer melt in the reservoir on time-dependent flow at 173.9°C is sum-
marized in Figure 5. For clarity the data from run 6 are not included in
this figure, although they should be considered with those plotted. All
samples had flow rates that leveled off to within 2% of 123×10^{-4} g/min
after extrusion for about 40 min. The points for run 9 are somewhat more
erratic than for other experiments, for reasons that are not clear.

With higher barrel loadings the time to reach the minimum in the flow
rate–time curve is longer. This agrees with Ballman's observations of a
polystyrene melt at 205°C with a constant-shear-rate piston-driven ex-
trusion rheometer.[8] There is otherwise no clear trend with varying height
of polymer in the reservoir, nor is there any evidence of a higher effective
shear stress at the orifice as the polystyrene drains from the reservoir. The
first signs of a very mild distortion of the extrudate occurred after 20 min of
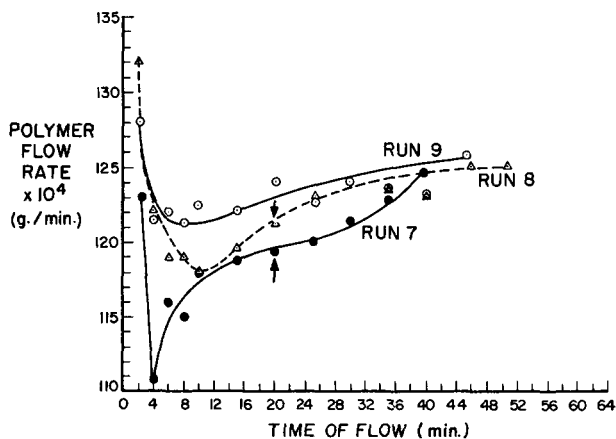flow in runs 5–9.

Fig. 5. Effect of reservoir drainage. Polymer loading above orifice: (run 7) 4.1 cm;
(run 8) 11.9 cm; (run 9) 12.6 cm.

Pretreatment without Shear

The standard pretreatment to this point has involved extrusion at stipulated shear stress and orifice dimensions after temperature equilibration at 216°C. One sample was pretreated without extrusion, to see whether this shearing had any pronounced effect on subsequent nonsteady flow at 173.9°C. This material was held in the viscometer for 15 min at 216°C and then removed, with the orifice, by pushing slowly from below. Its time-dependent flow behavior is shown in Figure 6. The shape of the flow rate–time curve is generally the same as that for other pretreated samples, but the long-term flow is slightly less, and the data points are more scattered. It seems likely, therefore, that the shear as well as the heat history can influence the time-dependent viscosity of polystyrene. Neither factor had a significant effect on the flow curve of the polymer at 173.9°C (Fig. 2).
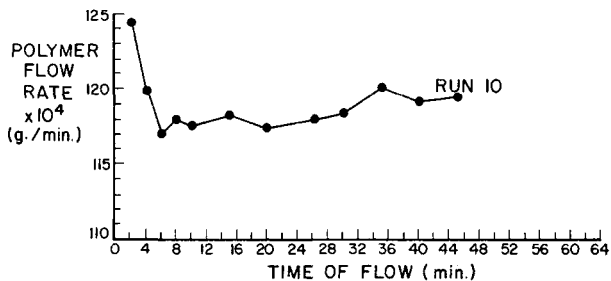

Fig. 6. Flow rate–time relation for polystyrene pretreated at 216°C without shear. Temperature 173.9°C. Orifice radius 0.035 cm, length 0.201 cm. Polymer loading 13.8 cm above orifice.

Melt Elasticity

A reasonable conjecture explaining the foregoing results would appear to be a change in the degree of entanglement of polymer chains with pretreatment. It might be expected, then, that manifestations of melt elasticity, such as swelling of the extrudate, would show changes paralleling the pronounced differences observed in nonsteady flow. This was not the case, however. Diameters of leading edges of extrudates were measured with a micrometer at room temperature. The ratio of extrudate to orifice diameters was about 1.5, whether or not the polystyrene had been pretreated. Neither the accuracy of the measurements nor the magnitudes of the differences between runs was sufficient to encourage any speculation about changes in entanglement density.

Nonsteady Flow at Higher Shear Stress

Time dependence of flow rates was measured with virgin and pretreated polystyrene at 2.40×10^6 dyn/cm² shear stress at the orifice wall. Extrudate distortion was severe at this shear stress. The data, plotted in

Figure 7, were erratic. Initial barrel loadings were the same for both samples, and the total weights extruded agreed within 5%. Nevertheless, the flow rate of the virgin sample decreased, and that of the pretreated sample increased slightly during the course of the experiment. There is, therefore, again no evidence of a clear reservoir drainage effect.

These results do not agree with Ballman's data on extrusion of a polystyrene sample at shear stresses in the "melt fracture" region.[8] Our experiments did not reveal a clear initial minimum in the flow rate (extrusion
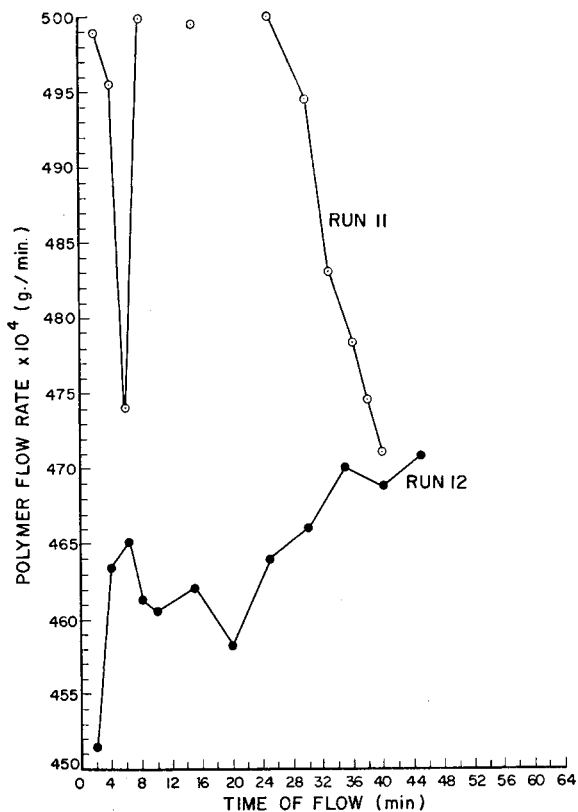

Fig. 7. Flow rate–time relation at higher shear stress: (run 11) virgin polystyrene; (run 12) pretreated as runs 7–9.

pressure peak in Ballman's apparatus) such as existed in preceding runs at lower shear stresses. Such a minimum probably occurred, but too quickly after the start of extrusion for detection by the technique used in this study. Ballman observed a progressively decreasing extrusion pressure as the polymer drained from the reservoir. This effect is evidently not present in the data in Figure 7, but only about 12% of the polystyrene was extruded in the present case, compared with complete drainage in Ballman's experiment.

DISCUSSION

The initial drop in output rate after application of shear stress in the capillary rheometer (Fig. 1) has been attributed to a time-dependent compressibility of the polymer melt in the rheometer reservoir.[8,20] It is assumed that after an abrupt increase of extrusion pressure a decrease in the free volume causes a gradual increase in the viscosity. A similar explanation has been offered for the initial decrease in shear rate when a constant torque is applied in a cone-and-plate viscometer.[21] It has been rejected, however, for the interpretation of the initial peak in shear stress in a similar instrument running at constant shear rate.[5] In this case the authors preferred an explanation involving changes in the nature of supermolecular rheological units, as suggested by Mooney.[22] A similar mechanism has been considered for the rheopectic behavior of some polymer solutions in constant shear-rate experiments.[7,23]

It is pertinent to note that this initial decrease in shear rate is not observed with all polymers. Devine[4] found such an effect with a polyisoprene compound but not with a heavily filled polychloroprene compound in which the "nerve," so called in rubber technology, was dead. Schrieber and Rudin[20] reported a similar difference between branched and linear polyethylene melts. The present work shows that this initial apparent increase in viscosity may be a function of melt history as well as of polymer type and experimental conditions.

Several mechanisms have been proposed to account for the longer term increase in apparent shear rate following the minimum (Figs. 1, 3, and 4). Frictional heating in the annular clearance between the piston or ball bearing and the reservoir wall[24] can be a contributing factor, but a number of experiments have shown that this effect alone cannot account for observations on polyethylene melts.[2,25]

The "reservoir effect" occurs because the viscometer barrel and capillary constitute a two-orifice series. As the reservoir drains, the associated pressure loss decreases, resulting in a progressively increasing shear stress at the capillary. Such an effect undoubtedly exists, but its magnitude must vary with changes in the mode of flow of the polymer in the reservoir. Calculations that have been made[26] are based on the implicit assumption of laminar, steady-state flow in both orifice and reservoir. This assumption is almost certainly invalid as a general rule for flow in the reservoir, where the polymer accelerates into the orifice. It is more surprising, therefore, that such calculations can account for some time-dependent viscosity effects[6] than that they fail to account completely for others.[1,2,4] The present results are an additional instance in the latter category. Pretreatment of the polymer did not change the equilibrium flow curve, from which the parameters for calculation of the magnitude of the reservoir effect are drawn,[6,26] but it did alter the nonsteady flow behavior significantly.

The increasing shear rate following the minimum in continuous capillary extrusion has also been attributed to a gradual disentanglement and orientation of polymer chains as a result of the shear stress.[3] Evidence has been

summarized showing the probable existence of this factor in the nonsteady flow of polyethylene.[1,2] It is unlikely, however, that the effects of pretreatment of the melt on the nonsteady flow of polystyrene reported above can be understood in terms of this mechanism.

In the same connection, it has been recommended that flow curve data in capillary viscometry be collected by proceeding from higher to lower and shear stresses, since this technique establishes steady-state orientation conditions more rapidly.[2] This procedure was followed in the present work; shear rate data obtained in a descending shear stress path were checked by repeating the measurements in an ascending order. The second set of shear rate figures were slightly higher, as expected, but only at the lowest shear stresses. Similarly, a flow curve determination starting at the lowest shear stress produced shear rates lower than those from the conventional method, at shear stresses lower than 2×10^6 dyn/cm^2. These differences amounted to less than 8%, even at the lowest shear stresses used, and were not significantly influenced by melt pretreatment. The effects are similar to those described by Schreiber for polyethylene[2] and ascribed to orientation or disentanglement of the polymer chains induced by the shear stress.

The various mechanisms mentioned briefly above are probably all real factors and must be considered in the nonsteady and equilibrium capillary viscometry of thermoplastics. None, however, accounts reasonably for the effects of melt history on the time-dependent flow of polystyrene. Another mechanism appears to be operative in this case and to be strongly interacting with the factors that have been recognized to this point. The most attractive current concept that can be applied qualitatively to the problem involves supermolecular flow units, as suggested by Mooney.[22,27] Such a flow unit is a melt domain, moving as a coherent mass in a continuous stress field. The size and nature of such domains is logically subject to shear and temperature-induced changes.

The erratic nonsteady flow recorded in Figure 3 may be due to nonuniformity of flow units, compared with that produced by pretreatment at a higher melt temperature. Heitmiller and his co-workers[28] have described similar changes in polyethylene viscosity following shear mixing. The viscosity was that measured by the melt index, which is not an equilibrium value for low melt index polymers.[1]

The quantitative interpretation of the nonsteady flow data must await the development of a technique for the production and characterization of reproducible flow units. This result has not been achieved in the present work or elsewhere, to our knowledge.

The unawareness of possible differences in the nature of flow units in various polymer samples may account for some of the discrepancies that have been reported in the measurement and interpretation of nonsteady flow of thermoplastic melts.[1,2] A number of workers have studied different polymers and observed dominant effects that could be understood in terms of one or other mechanism to the exclusion of others. The present report, in which nonsteady flow has been varied independently of the poly-

mer and measurement conditions, illustrates the wisdom of caution in the extrapolation of interpretations from any one series of experiments. It would be useful to reexamine some of the polymers that have been studied heretofore with this factor in mind. For example, Marshall and Riley[6] obtained data with plasticized poly(vinyl chloride), in which the long-term increase in flow rate could be accounted for by the "reservoir effect" calculations mentioned above. Recently Berens and Folt[29] reported that changes in the melt flow of this polymer result from thermal and mechanical treatment. The nonsteady flow behavior probably is also changed by these treatments which, the authors suggest, change the size and nature of supermolecular flow units.

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