

Fig. 4. Flow rate vs. time since start of extrusion of polyethylene samples: (G, H) High-density, linear polyethylenes; (I, J) low-density polyethylenes. Arrow indicates time at which excess pressure was applied.

The result is an initially high viscosity which decreases as the melt expands elastically.

The increasing outputs following the minima shown in the upper curves in Figures 1-3 are more likely associated with a gradual reduction in the effectiveness of chain entanglement and alignment of the polymer chains along flow lines into the orifice.⁴ This would tend to reduce F , resulting in a decreased viscosity.

The effects of polyethylene type were investigated, briefly, with the results given in Figure 4. The study included two low-density polyethylenes (dashed curves) and two high density polyethylenes (solid curves). Polymer flow rates were measured from application of the normal load until a steady flow rate had apparently been reached. An excess load was applied to drive the piston down 1 in., the extra load was released, and measurement of output rates was continued. The low-density polymers exhibited the same behavior as similar materials in preceding examples but the linear polyethylenes behaved quite differently. A decrease in output when the load was first applied was not detected. Application and removal of an excess load resulted in increased outputs, which persisted at their higher levels. Evidently the linear polyethylenes had a lower capacity for storage of elastic strain energy than the branched resins.

In the operation of extrusion viscometers the volume swept out by a piston is often equated to the volume of polymer extruded, assuming that the melt is essentially incompressible. The foregoing data indicate that this practice can sometimes be misleading and that the errors involved will probably depend on the extrusion system, temperature, shear rate, and polymer. Marker, Early, and Aggarwal⁵ have made this assumption in an interesting recent paper which also reports a time drift in output rates from a melt indexer. This effect is ascribed to frictional heating of the polymer between the piston and cylinder wall. We intend to discuss this alternate way of interpreting time drifts in rates of shear in a forthcoming publication.

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The Second-Order Transition Phenomena in Polyethylene

Many values have been suggested for the second-order transition temperature of polyethylene by different authors, but none of these has discussed which value is the true second-order transition point and what the nature of the other points is.

We have conducted some dilatometric measurements on polyethylene in the temperature range from -76 to $+28^{\circ}$ C., using *n*-propyl alcohol as the filling liquid. Some of our results can be used for discussing the present problem.

The difference between the specific volume of quenched Marlex 50/15 (M_q) and that of annealed Marlex 50/15 (M_a) is shown in Figure 1. It is seen that this value does not

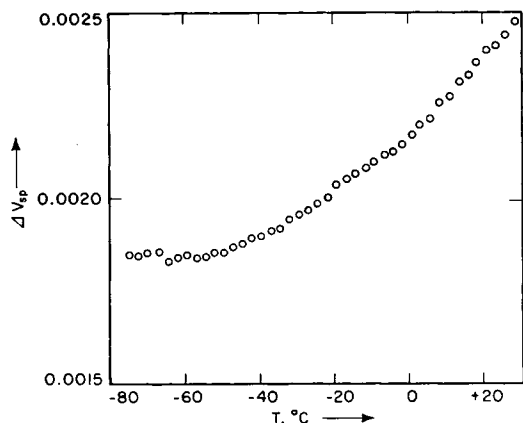


Fig. 1. The difference between the specific volumes of quenched and annealed Marlex 50/15.

change with temperature below -55°C . This means that in this range

$$dV_c/dT = dV_a/dT$$

where V_c is the specific volume of the pure crystalline phase and V_a of pure amorphous phase.¹ So it may be said this temperature is the second-order transition point of Marlex.

The crystallinity of crystalline polymer is usually defined from dilatometric data as

$$\theta = (V - V_c)/(V_a - V_c)$$

If the measurement is carried out on three samples, each having a different crystallinity, the relation

$$(\theta_1 - \theta_0)/(\theta_2 - \theta_0) = (V_1 - V_0)/(V_2 - V_0)$$

holds at any temperature so long as each V_a and V_c is the single value function of temperature, even if there are some discontinuous points. If the crystallinity does not change with temperature, the right side of this equation must be a constant which is independent of temperature. On the other hand, if the right side of this equation changes with temperature, the crystallinity changes with temperature.

Calculating the value

$$[V(M_n) - V(M_a)]/[V(M_q) - V(M_a)]$$

from our data, we obtained the plot shown in Figure 2. It is seen that this value changes with temperature above -30°C ., and the crystallinity of this polyethylene can be said to change with temperature, at least above this point. The value -21°C ., reported by Danusso and others² as

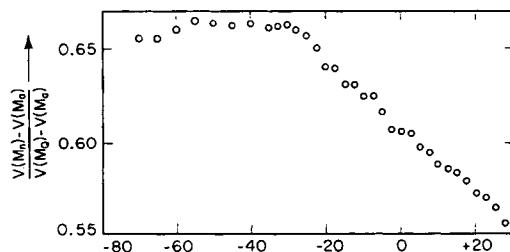


Fig. 2. Test of crystallinity change.

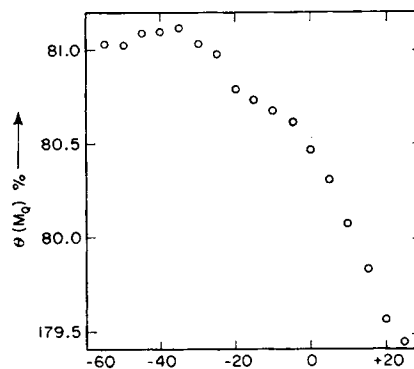


Fig. 3. Change of crystallinity of quenched Marlex 50/15 with temperature.

the second-order transition point of polyethylene, may correspond to the beginning of this crystallinity change, the temperature being shifted by some factor introduced in their experimental data.

The crystallinity change of our sample M_q can be calculated by adopting as the first-order approximation the method of Hoffman and Weeks³ and applying some additional calculations. The results of our calculations are shown in Figure 3.

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