meaning of this apparent correlation is not clear without further investigation.

In a separate experiment, a sheet 0.020 in. thick was molded at 1000 atm in the large mold and cut into strips which were run in a conventional glass dilatometer filled with degassed mercury and heated at 0.5°C/min. After cooling overnight, it was rerun as its own control. The results are shown in Figure 12. The volume compaction effect relaxed out most rapidly in the region 80–90°C, which, allowing for the difference in heating rates, corresponds with the onset of the exotherm in DTA. Thus, the exothermic relaxation is accompanied by a dilational volumetric relaxation.

In sum, then, a thermally induced dilational and exothermic relaxation is seen in the pressure-compacted samples, starting below T_g and continuing through the glass transition. Increasing the molding pressure has little effect on the intensity of the exotherm (the height of the peak), but moves the onset of relaxation to lower temperatures. Aging of the samples moves the onset back to higher temperatures. The effect of high-pressure molding on these properties seems to reach a limit around 3000 atm.

SORPTION OF SOLVENT VAPOR

Sheets about 0.010 in. thick were molded in the small mold at 3000 atm. Sorption of methyl ketone vapor (MEK) was monitored using a quartz-helix balance thermostatted at 25°C and a vapor pressure of 50 mm Hg.
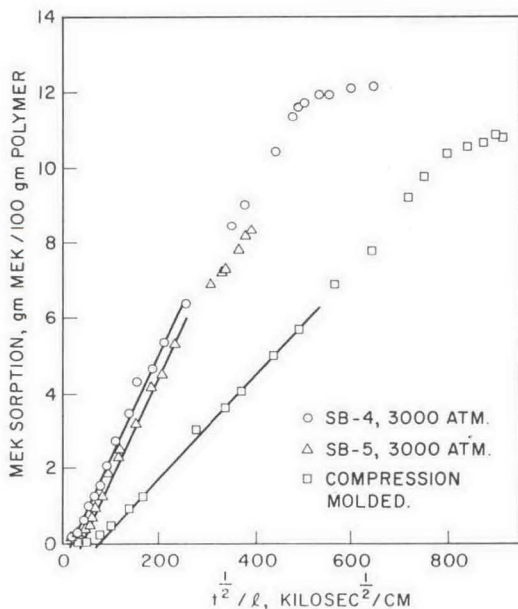

Fig. 13. Sorption of methyl ethyl ketone vapor at 25°C and 50 mm Hg pressure by polystyrene glasses vitrified at (O,Δ) 3000 atm and (□) compression-molded control.

In Figure 13, the percentage gain in sample weight is plotted against the square root of time divided by the sample thickness. Integration of Fick's second law under these conditions[25] predicts that the plot should be linear up to 60–70% of the equilibrium weight increase and that the square of the slope should be proportional to the diffusion coefficient, which is assumed to be a constant. Although the diffusion coefficient in the present samples is known to be strongly dependent on the local concentration of MEK, it is seen that the plots are linear up to about one half of the final value. From the slope of the straight-line portions, apparent (average) diffusion coefficients may be calculated to be: $10 \times 10^{-10} \text{cm}^2/\text{sec}$ for the pressure-compacted samples and $3.2 \times 10^{-10} \text{cm}^2/\text{sec}$ for the control.

Departure from Fickian diffusion kinetics is seen, however, at the short-time end of the curves, where the Fickian treatment predicts that the straight-line portion should pass through the origin. Instead, an induction period is observed corresponding to about 1.2 hr for the control and 0.1 hr for the high-pressure samples. The Fickian diffusion process assumes instantaneous equilibrium between vapor and polymer at the surface. However, in the dry polymer well below T_g, both the solubility and diffusion coefficients are quite small compared to the same properties in the polymer plasticized by 10% MEK. Hence the sorption process starts slowly until the polymer surface has relaxed enough to absorb the equilibrium amount of penetrant vapor. In this sense, the induction period is a measure of the rate at which the samples are relaxed by solvent vapor,[25–28] and it is seen that the pressure-compacted samples are relaxed far more rapidly. The aging effect also is seen in these data; the SB-4 sample, on which measurements were started about three days after molding, is seen to have a longer induction period than the SB-5 sample, on which measurements were started only a few hours after molding.

PERMEATION AND SOLUTION OF INERT GASES

Concurrent studies of the permeation behavior of simple gases in these same samples have shown that the permeability coefficient of argon is decreased by more than half in a sample molded at 1000 atm.[22] The gas solubility coefficient passes through a minimum at a molding pressure around 1000 atm, which corresponds fairly well to the present observed maximum in yield stress and the first appearance of the exothermic relaxation. The solubility coefficient can be related to the total volume of microvoids or packing defects available to the gas for solution, and this available volume fraction must pass through a similar minimum. Since the diffusion coefficient shows a monotonic decrease with increasing molding pressure, these defects are interpreted to exist in regions of high local void volume, which, however, constitute only a small fraction of the total polymer volume.

Increasing the molding pressure up to about 1000 atm reduces the number of chain-packing defects and produces a stronger, more coherent