

Fig. 11. Effect of vitrification pressure on temperature at which exothermic relaxation first appears in thermogram. Data are for DTA heating rate of  $10^{\circ}\text{C}/\text{min}$  on samples 2-3 days after molding.

point, a 3000-atm molding was run using a previously run (i.e., relaxed) polystyrene sample of similar weight in the reference pan in place of the usual glass beads. The result is shown in Figure 8, where the general shape of the exotherm is seen quite clearly. To confirm that this was a continuing broad exotherm, a 3000-atm molding was run until the exothermic onset was clearly seen and the heating control was switched to "hold." The sample was held near  $80^{\circ}\text{C}$  for 5 min, then cooled, and rerun, as shown in Figure 9. The remainder of the exotherm is clearly seen, with the onset now shifted upward to about  $95^{\circ}\text{C}$ , some  $15^{\circ}\text{C}$  above the temperature at which the sample was relaxed.

Early in this phase of the work, a previously unused scrap of a six-month-old 3000-atm molding was retrieved and run. Comparison of this aged sample with a three-day-old sample molded at the same pressure is shown in Figure 10. The onset of the exotherm is seen to be some  $15^{\circ}\text{C}$  higher in the older sample. Also an endothermic inflection preceding the exotherm is seen, especially in the older sample. A corresponding effect of sample age also has been seen in density changes<sup>3</sup> and in solubility coefficients of simple gases.<sup>22</sup> The data of Figure 10 indicate that the effects of high-pressure treatment affect the relaxation process for long periods of time; even after six months at ambient conditions, considerable memory of the high-pressure history remains.

In Figure 11, the onset temperature of the exothermic relaxation is plotted against molding pressure over the range of 1000 to 5000 atm. It is seen that  $T_r$  decreased rather uniformly at about  $10^{\circ}\text{C}/\text{kbar}$  (c.f.,  $30^{\circ}\text{C}/\text{kbar}$  for  $dT_g/dP$ ) over the range of 1000 to 3000 atm. Thereafter,  $T_r$  was virtually unchanged as the molding pressure was raised further to

5000 atm, even though  $T_r$  was still some 40°C above room temperature. Visually, the thermograms of the 5000-atm samples were not readily distinguishable from those of the 3000-atm samples.

The curve in Figure 11 may be thought of as defining a region (above and to the right of the data points) in which an additional relaxation process, not directly related to the glass transition, is possible. The location of the break in the curve around 70°C and 3000 atm is interesting, if only a coincidence. In tensile tests of polystyrene under elevated

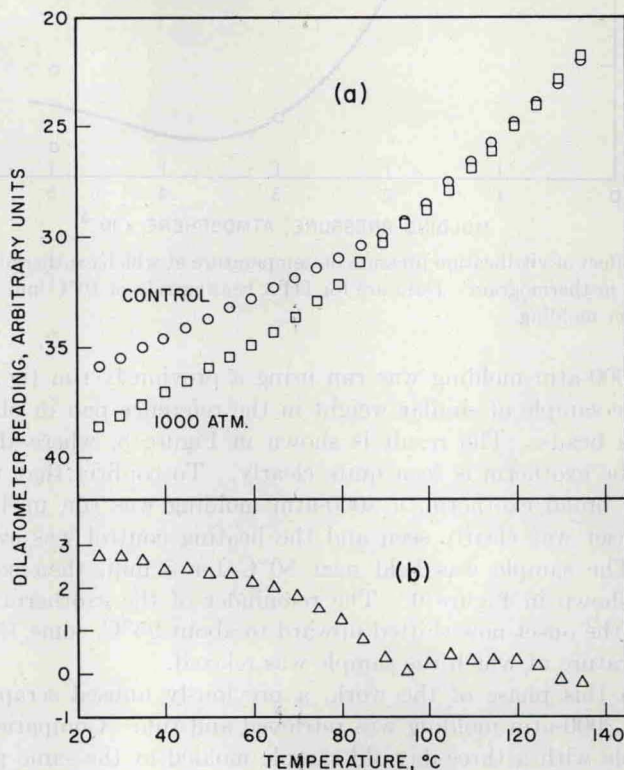


Fig. 12. (a) Dilatometric expansion of ( $\square$ ) polystyrene vitrified at 1000 atm and ( $\circ$ ) reheat control. Heating rate was 0.5°C/min. (b) Volume compaction from difference of curves in (a). One division represents approximately 0.37% difference in volume.

pressures at room temperature, Biglione and co-workers<sup>12</sup> found ductile failure at 3000 atm and above; the normal brittle failure occurred at pressures below this. This pressure compaction measured by Rehage and Breuer<sup>9</sup> showed little or no further increase as the vitrification pressure was increased from 3000 to 6000 atm. The temperature coordinate of the break in Figure 11 is a reasonable approximation of the ductile-brittle transition of polystyrene in normal tensile testing and is slightly above the small secondary transition near 50°C found by several workers,<sup>23,24</sup> probably associated with a partial vibration of the phenyl ring. The