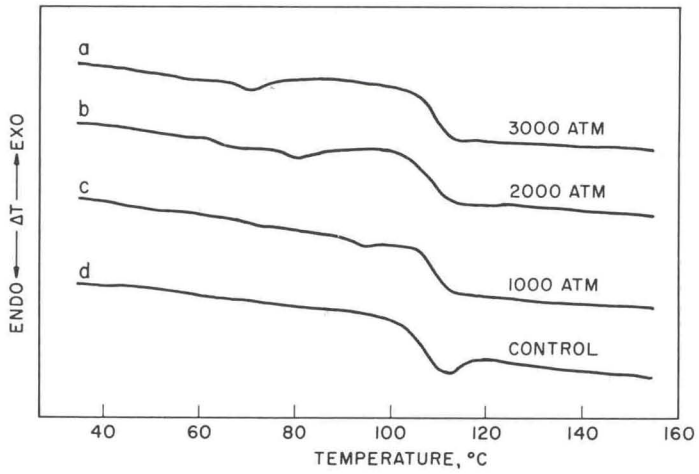

Fig. 7. Differential thermograms of polystyrene glasses vitrified at (a) 3000 atm; (b) 2000 atm; (c) 1000 atm; (d) control. Heating rate was 10°C/min.

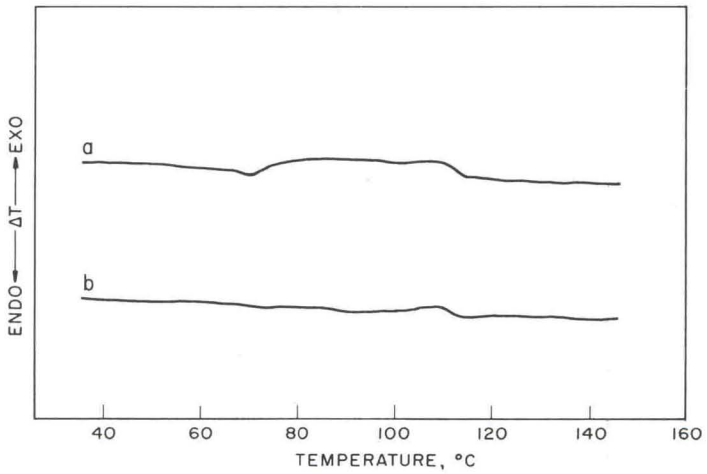

Fig. 8. Differential thermogram of (a) polystyrene vitrified at 3000 atm in sample pan with ordinary polystyrene molding in reference pan; (b) reheat control.

temperature to about 150°C, usually at 10°C/min. The sample was then cooled and rerun to serve as its own control.

A series of thermograms for these moldings is shown in Figure 7. It is seen that the principal effect of the high molding pressure was to induce a low broad exotherm which started at some temperature (designated T_r) below T_g and continued through the glass transition. The glass transition temperature itself, as revealed by the drop in the baseline, cannot be said to change, although any subtle shift would be masked by the change in shape of the thermogram. The extrapolated onset technique was used to determine T_r and T_g. Runs at 20°C/min and 5°C/min were somewhat

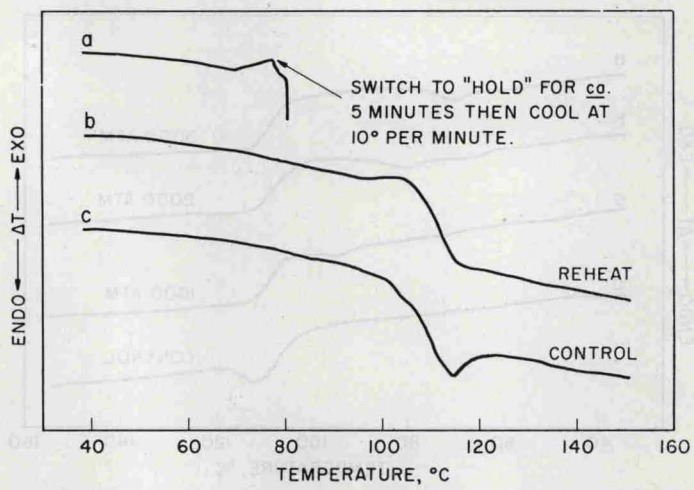

Fig. 9. "Interrupted" thermogram of polystyrene vitrified at 3000 atm. Sample was: (a) heated at 10°C/min into region where exotherm had started, held at 80°C for ca. 5 min, and cooled at 10°/min; (b) then reheated at 20°/min to 150° and cooled again; (c) reheated at 20°/min as a control.

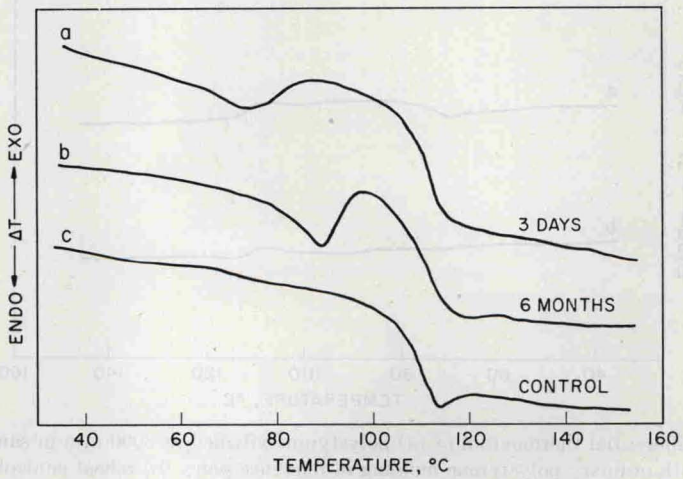

Fig. 10. Differential thermograms of polystyrene vitrified at 3000 atm, taken (a) three days and (b) six months after molding; (c) control. Heating rate here was 20°C/min.

more difficult to read than the runs at 10°C/min shown, and the results were not well suited to quantitative analysis of heating rate effects. It did appear, however, that T_r was somewhat more sensitive to heating rate than was T_g.

Because it is somewhat unusual for a first-order thermodynamic effect to produce such a low broad peak, an alternative interpretation was entertained that the shift designated T_r might be a "secondary" transition (e.g., from one quasi-stable glass phase to another). To investigate this