



Fig. 6. Effect of vitrification pressure on maximum relaxation index following compressive yield in polystyrene glasses.

A major point of interest was how the yield stress would be changed by high-pressure molding treatment. Volumetric considerations¹⁴ and such interpretations of yielding as Whitney's, based on defect mobility,^{15,16} would predict an increase in yield stress as the molding pressure increased. On the other hand, conformational considerations, such as used in Robertson's interpretation of the yielding process,¹⁷ would predict a reduction in yield stress at higher molding pressures since the polymer is frozen into a conformation characteristic of a higher temperature than that for the normal T_g . The observed behavior of yield strength with molding pressure followed neither of these predictions entirely, but showed a maximum in the region around 1000 atm, as seen in Figure 3.

Typical stress-strain curves are shown for a high-pressure sample and a control in Figure 4, where it is seen that the major difference is that the yield peak for the high-pressure sample was "sharper" and narrower than that for the control. This sort of difference does not lend itself to a description in terms of conventional stress-strain parameters. We have employed the technique, common in metallurgical mechanics, of decomposing the strain into elastic and plastic components. As indicated in Figure 4 for the strain at the point of maximum load, the elastic strain

may be represented as the stress at the point of interest divided by the elastic modulus. The plastic strain, then, is the difference between the (observed) total strain and the elastic strain.¹⁸ When the yield strains of the present samples were decomposed in this fashion, the results were as shown for a typical set of data in Figure 5. The total strain at yield is seen to decrease monotonically as the molding pressure increased, but the change is seen to be almost entirely in the plastic strain, which decreased by one third of its original value.

Additional information may be estimated from the rate with which the load fell from the maximum at the yield point. In the present case, the drop in load must reflect a true softening or relaxation of the material. Since the stress field was compressive and no decrease in cross-sectional area was involved, the true stress must have decreased by at least as much as did the engineering stress. Also, it is known from photographic studies of poly(methyl methacrylate) in tension¹⁹ that the geometric instability (neck or bulge) does not form concurrently with the maximum in load, but definitely later. At the point of greatest (downward) slope of the load-compression curve, the change in cross-sectional area was not more than 10-20%. The downslope is conveniently expressed as a relaxation rate per unit time or per unit strain. The latter form is plotted against molding pressure in Figure 6, where it is seen that this relaxation rate varied markedly with molding pressure, being greatest in the 2000-atm molding. The more than twofold change in relaxation rate was much larger than could be accounted for on the basis of geometric factors alone and indicates that the relaxation rate of the bulk material must be changing. In general, a relaxation rate should be a strong function of the original load. Reference to Figure 3 reveals the fortunate fact that there are two pairs of moldings with approximately the same yield stresses, viz., 50 atm versus 3000 atm, and 1000 atm versus 2000 atm. Comparison of the corresponding relaxation rates shows that in both cases relaxation was faster in the sample with the higher molding pressure, after the effect of original load was taken into account.

Yielding in polymers has been regarded as a stress- or strain-induced transition similar to the glass transition,^{20,21} which makes large-scale relaxation possible. Since the relaxation induced by strain was found to be more rapid in the samples molded at higher pressure, it is of interest to examine the relaxation behavior induced by more conventional means, specifically heat and solvent vapor treatments.

DIFFERENTIAL THERMAL ANALYSIS

Sheets about 0.010 in. thick were molded from 200°C in the 1-in. mold at 3000, 2000, and 1000 atm. Additional samples were molded at 250°C and 5000 atm using the 1-in. mold in a 150-ton capacity press, and by molding a 0.020-in.-high slug in the high-pressure dilatometer. From the sheets, 1/4-in. discs were punched out with a paper punch and run in the calorimeter cell of a du Pont 900 differential thermal analyzer from room