

## Mechanical and Relaxation Properties of Polystyrene Molded at High Pressures

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### Synopsis

Atactic polystyrene glasses were molded at high pressures by cooling the polymer melt at pressures up to 5000 atm. Changes found in the properties of the samples included: a lower mechanical damping factor at temperatures from 50°K to 300°K; a higher compressive elastic modulus; a maximum in compressive yield stress at a molding pressure around 1000 atm; faster relaxation at yield; appearance of an exothermic dilational relaxation below  $T_g$  when the samples were heated; and faster relaxation in methyl ethyl ketone vapor. The observed behavior is interpreted in terms of a model based on pressure-induced heterogeneities in local order. The initial effect of increased molding pressure is to produce a more compact polymer which has less segmental mobility and more extensive interchain forces. Above molding pressures of about 1000 atm, a second effect develops due to the apparent formation of localized conformations which are stable under the high-pressure vitrification conditions, but not at room conditions. The spontaneous decay of these high-energy regions leads to subsequent formation of microvoid defects and more rapid structural relaxation effects. The existence of an optimum molding pressure somewhat below 1000 atm is indicated for polystyrene.

### INTRODUCTION

In the last few years, there has been an increasingly frequent application of high-pressure technology to the characterization of high polymers.<sup>1</sup> The majority of these studies have been concerned with the behavior of polymers while under hydrostatic pressure, and the emphasis has been on relaxation phenomena. A related field is the study at atmospheric pressure of polymers which have been subjected to a high-pressure history—this technique has been used successfully to investigate thermodynamic parameters and morphology of crystalline polymers. By contrast, only a few introductory studies<sup>2-7</sup> have been made on the effects of a high-pressure history on the properties and structure of amorphous polymers. These investigations have concentrated almost entirely on the residual density increase or “pressure compaction” effect and on its relaxation on heating or annealing.

The present study was undertaken to characterize the effects of a high-pressure history on an amorphous polymer by a wider variety of methods than have been used previously in order to establish property-structure relationships suitable for this potentially useful method of

polymer modification. Polystyrene was chosen for the initial investigation because the noncrystallizable atactic form is easily characterized and the glass transition is well above room temperature. The samples were prepared by cooling the polymer melt to room temperature under constant pressures up to 5000 atm (5 kilobars) to form a glass. The pressure was then released and the sample was removed and tested by a number of different mechanical and physical techniques.

The pressure at which a polymer vitrifies can be expected to have a major effect on the local chain conformation. The variation in molding pressure can also lead to significant effects on several properties of immediate practical importance. Modern extruders can generate pressures in the barrel which approach 10,000 psi (670 atm), although the polymer is not at this pressure when it vitrifies. A conventional compression molding subjects the polymer to a pressure on the order of 50 atm. It will be seen that even the relatively modest changes in molding pressure obtained by conventional apparatus can produce significant changes in sample properties.

### SAMPLE PREPARATION

The polymer used was Dow Styron 690, a thermally polymerized atactic polystyrene nominally free of additives. The intrinsic viscosity measured in toluene at 25°C was 0.88 (g/100 cc)<sup>-1</sup>, corresponding to  $M_v \approx 240,000$ . The glass transition temperature at atmospheric pressure was 96°C, measured in a conventional glass dilatometer. The glass transition at high pressure was measured using a high-pressure steel dilatometer described elsewhere.<sup>8</sup> Over the range of 1 to 1700 atm, the  $T_g$  increased at the rate of 30°C/kbar. This was quite consistent with the literature reports<sup>1,5,6,9</sup> that the  $T_g$  of polystyrene increases at an initial rate of 25°–30°C/kbar and at a lower rate of about 15°C/kbar at higher pressures in the range of 4 to 6 kbars.<sup>9</sup>

Small samples were prepared in a 1-in. diameter mold designed for mounting metallurgical specimens for polishing. A common 40,000-lb capacity compression-molding press could produce pressures higher than 3000 atm on the 1-in. sample. For tests requiring larger samples, a mold was designed and built to produce discs 3<sup>3</sup>/<sub>8</sub> in. in diameter at pressures up to 5000 atm. The molding faces could be reproducibly realigned relative to each other to within ±0.001 in. over the entire face area, so that the thickness of a given molding was quite uniform from point to point. The large mold was evacuated during heating to devolatilize the polymer and protect the sample against oxidative degradation.

The samples were molded as sheets or slabs of different thicknesses. The appropriate amount of polymer was heated in the mold under no load, then a small load was applied to deform the polymer and fill the available space. The pressure was then raised to the desired high-pressure level over a period of about 1 min. After an appropriate dwell time under pressure as discussed below, the heater was shut off and the mold was

cooled in free air at a few degrees per minute, under constant pressure. When the mold had cooled below 30°C, the pressure was released and the sample was removed and, except where noted, conditioned in room air for at least 48 hr before being tested.

The dwell times of 3–15 min for the polymer under pressure at the high molding temperature were calculated to be at least one order of magnitude longer than the relaxation time,  $\tau$ , predicted by the WLF equation. The absence of birefringence in the plane of the cooled samples indicated that the dwell times were sufficient for relaxation under the conditions used. None of the samples showed discoloration, monomer odor, or other signs of degradation, and moldings at 3000 atm in the high-pressure dilatometer showed no decrease in solution viscosity. The density of the high-pressure moldings was about 1% greater than that of the controls, but the scatter was greater than permissible for use as a characterization parameter.

### MECHANICAL DAMPING SPECTRUM

The mechanical damping spectrum of a strip of a 0.015-in.-thick sample, molded from 200°C at 3000 atm, was measured from 4.2°K to 300°K at a frequency of about 2 Hz, using a high-sensitivity cryogenic torsional pendulum built by Armeniades et al.<sup>10</sup> The oscillations were quite small, being less than one angular degree to each side of the equilibrium position. The damping spectra of this sample and of a compression-molded control sample are shown in Figure 1. The high-pressure sample exhibited a damping factor which was about 10% lower than the control over most of the temperature range studied. This is indicative of a more rigidly bound structure which stores more energy in elastic deformation and

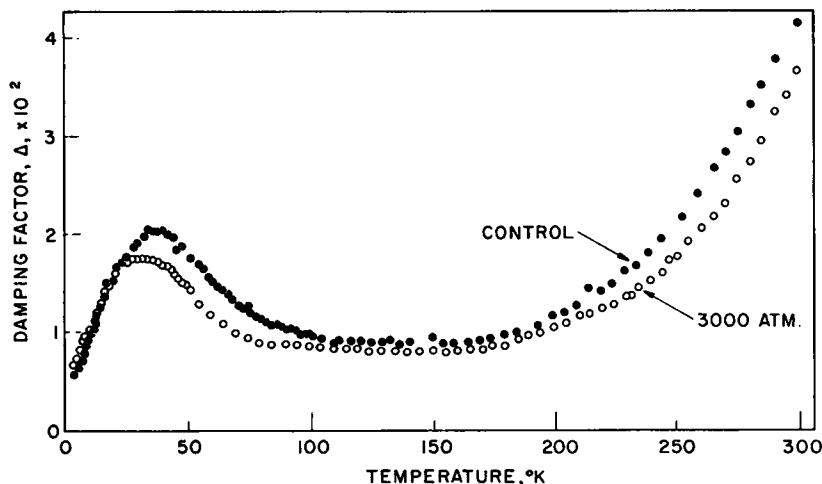


Fig. 1. Cryogenic mechanical relaxation spectrum of polystyrene glasses molded (○) at 3000 atmospheres, and (●) compression-molded control. Torsional pendulum frequency was 1–2 Hz.

dissipates less energy in independent segmental motion. Matsuoka and Maxwell<sup>11</sup> found a similar decrease in the mechanical loss factor of polyethylene and polypropylene molded under pressures in the kilobar range, but attributed this only to the increased crystallinity of their polymers.

### COMPRESSIVE STRESS-STRAIN TESTS

Plaques  $\frac{1}{4}$  in. thick were molded from 200°C at various pressures, and cylinders 0.230 in. in diameter and 0.500 in. long were turned down from them on a turret lathe. The surface finishes were smooth to the touch, but still cloudy visually. The tests were performed using a cross-over-type jig in an Instron testing machine, and the strains were corrected for deflection of the jig and machine.

A summary of the stress-strain results is listed in Table I. It will be noted that a given property at various strain rates shows considerable scatter, probably due to difficulties in calibrating the machine reproducibly on different days. Therefore, presentation of data from different strain rates serves here only as a check on the reproducible behavior of different molding pressures.

The compressive elastic modulus is shown as a function of molding pressure in Figure 2. It is seen that the modulus increased by roughly 10% as the molding pressure was raised from 50 to 1000 atm, and remained

TABLE I  
Summary of Compressive Stress-Strain Properties of Polystyrene Molded at High Pressures<sup>a</sup>

Strain rate, sec <sup>-1</sup>	Molding pressure, atm	Elastic modulus, psi $\times 10^{-3}$	Yield stress, psi $\times 10^{-3}$	Yield strain, %	Maximum relaxation index, <sup>b</sup> psi $\times 10^{-3}$
$0.67 \times 10^{-3}$	50	450 $\pm$ 4	13.7 $\pm$ 1	4.51 $\pm$ .04	130 $\pm$ 3
	1000	500 $\pm$ 9	14.8 $\pm$ .2	4.17 $\pm$ .04	264 $\pm$ 13
	2000	496 $\pm$ 9	14.5 $\pm$ .1	4.09 $\pm$ .05	333 $\pm$ 2
	3000	495 $\pm$ 13	13.6 $\pm$ .1	3.87 $\pm$ .04	265 $\pm$ 10
$1.67 \times 10^{-3}$	50	459 $\pm$ 6	14.8 $\pm$ .1	4.70 $\pm$ .05	161 $\pm$ 4
	1000	497 $\pm$ 5	15.9 $\pm$ .1	4.41 $\pm$ .04	317 $\pm$ 11
	2000	514 $\pm$ 12	15.8 $\pm$ .2	4.18 $\pm$ .04	401 $\pm$ 8
	3000	505 $\pm$ 2	14.7 $\pm$ .1	4.00 $\pm$ .08	321 $\pm$ 9
$3.3 \times 10^{-3}$	50	453 $\pm$ 11	14.7 $\pm$ .1	4.67 $\pm$ .02	166 $\pm$ 4
	1000	495 $\pm$ 11	15.8 $\pm$ .2	4.40 $\pm$ .04	339 $\pm$ 8
	2000	498 $\pm$ 17	15.5 $\pm$ .2	4.26 $\pm$ .06	444 $\pm$ 17
	3000	501 $\pm$ 8	14.8 $\pm$ .1	4.06 $\pm$ .07	346 $\pm$ 10
$6.7 \times 10^{-3}$	50	477 $\pm$ 32	14.8 $\pm$ .4	4.66 $\pm$ .15	176 $\pm$ 8
	1000	510 $\pm$ 27	15.9 $\pm$ .6	4.26 $\pm$ .14	349 $\pm$ 5
	2000	521 $\pm$ 36	15.9 $\pm$ .5	4.20 $\pm$ .10	451 $\pm$ 28
	3000	507 $\pm$ 12	14.9 $\pm$ .3	3.98 $\pm$ .07	366 $\pm$ 19

<sup>a</sup> Results are in the form: mean of five specimens  $\pm$  one standard deviation.

<sup>b</sup> Greatest (negative) slope after maximum at yield expressed as psi per unit sample strain.

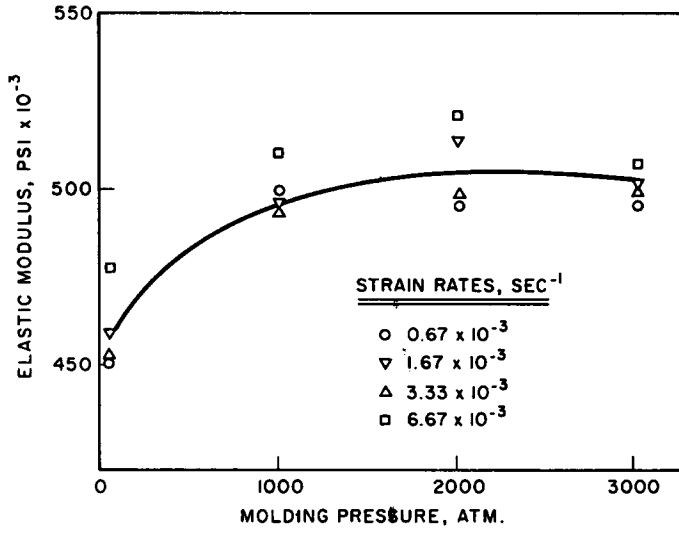


Fig. 2. Effect of vitrification pressure on compressive elastic modulus of polystyrene glasses.

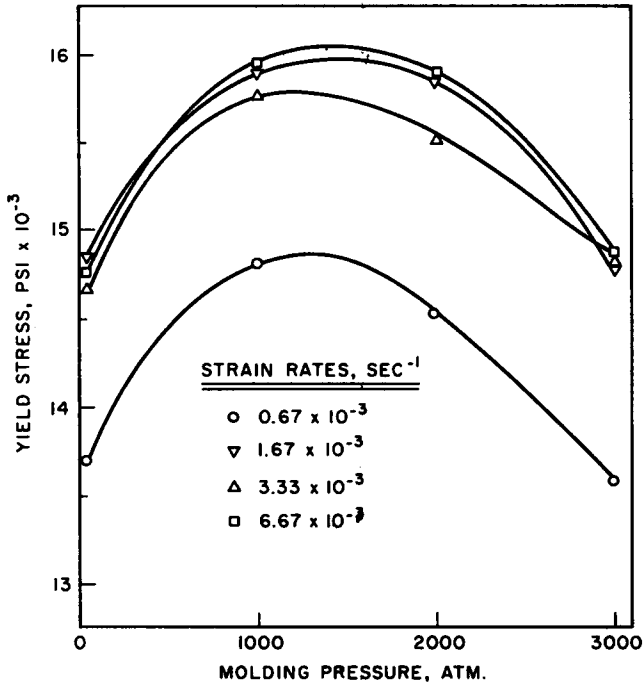


Fig. 3. Effect of vitrification pressure on compressive yield stress of polystyrene glasses.

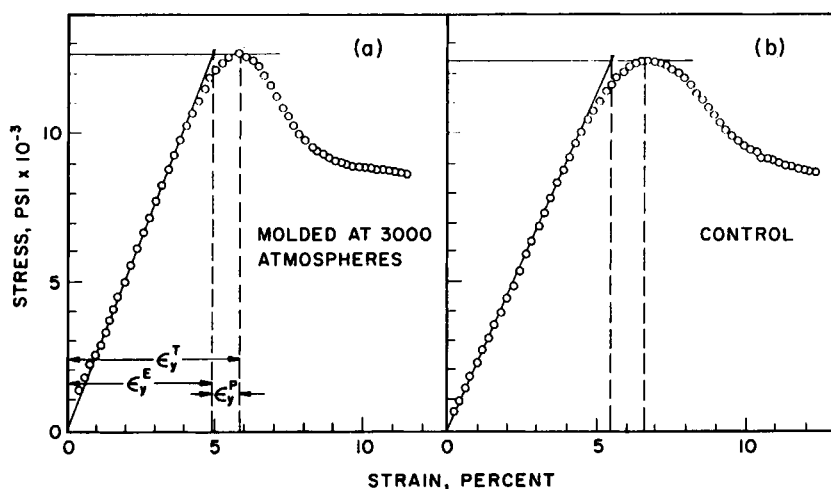


Fig. 4. Typical compressive stress-strain curves for polystyrene glasses: (a) molded at 3000 atmospheres; (b) compression-molded control. Separation of yield strain into  $\epsilon_y^E$  and  $\epsilon_y^P$  is explained in text.

approximately constant thereafter as the molding pressure was raised further. The increase in modulus is indicative of a more compact, strongly bound glass produced at high pressures. Moduli are also increased by treatments that reduce the volume of the sample in more conventional ways, such as by cooling or testing under hydrostatic pressure.<sup>12,13</sup>

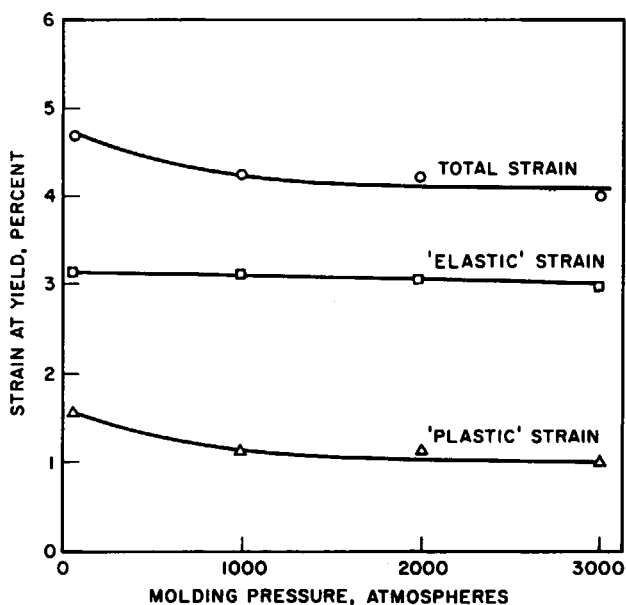


Fig. 5. Typical effect of vitrification pressure on strain at compressive yield of polystyrene glasses. Strain rate for data shown was  $6.67 \times 10^{-3} \text{ sec}^{-1}$ .

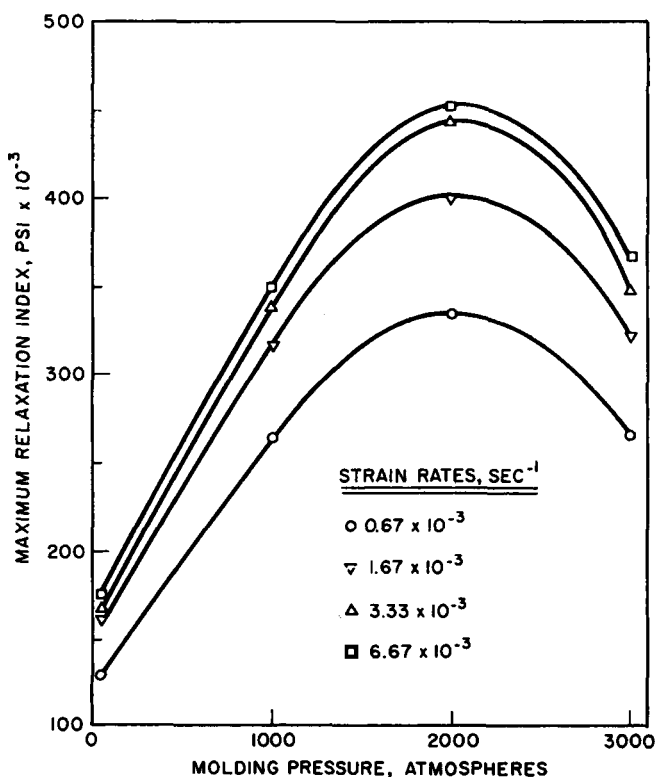


Fig. 6. Effect of vitrification pressure on maximum relaxation index following compressive yield in polystyrene glasses.

A major point of interest was how the yield stress would be changed by high-pressure molding treatment. Volumetric considerations<sup>14</sup> and such interpretations of yielding as Whitney's, based on defect mobility,<sup>15,16</sup> 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,<sup>17</sup> 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.<sup>18</sup> 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 tension<sup>19</sup> 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,<sup>20,21</sup> 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



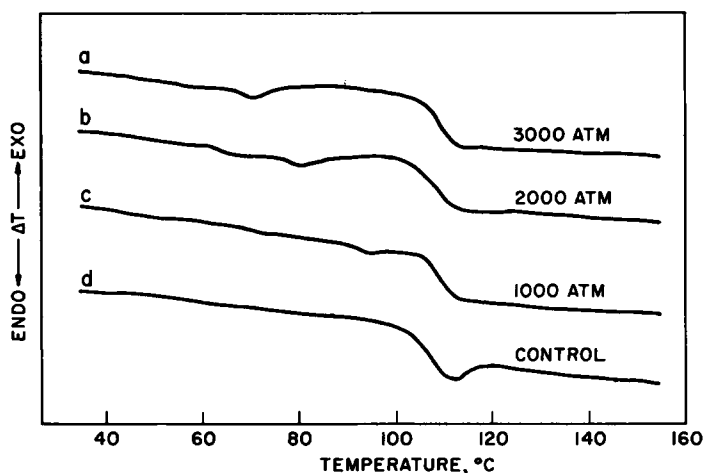


Fig. 7. Differential thermograms of polystyrene glasses vitrified at (a) 3000 atm; (b) 2000 atm; (c) 1000 atm; (d) control. Heating rate was  $10^{\circ}\text{C}/\text{min}$ .

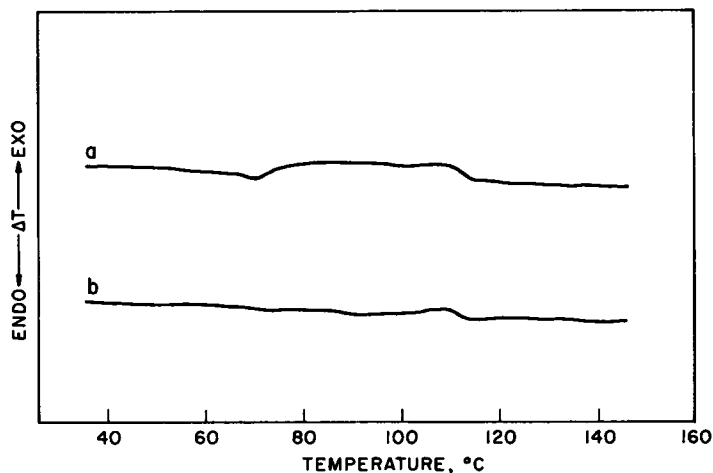


Fig. 8. Differential thermogram of (a) polystyrene vitrified at 3000 atm in sample pan with ordinary polystyrene molding in reference pan; (b) reheat control.

temperature to about  $150^{\circ}\text{C}$ , usually at  $10^{\circ}\text{C}/\text{min}$ . 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  $T_i$ ) 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  $T_i$  and  $T_g$ . Runs at  $20^{\circ}\text{C}/\text{min}$  and  $5^{\circ}\text{C}/\text{min}$  were somewhat

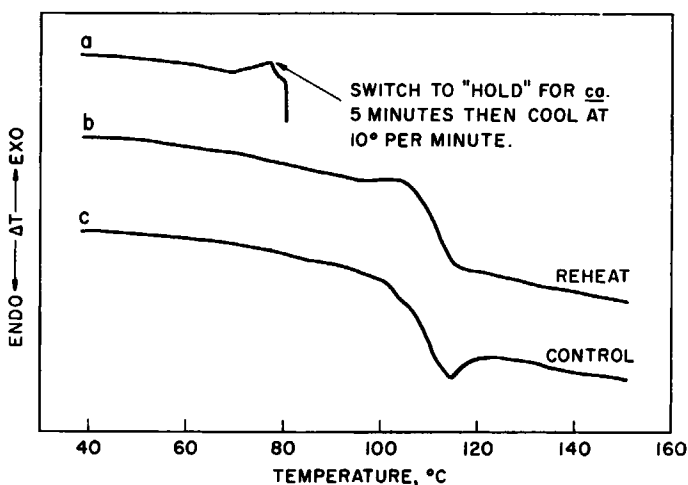


Fig. 9. "Interrupted" thermogram of polystyrene vitrified at 3000 atm. Sample was: (a) heated at  $10^{\circ}\text{C}/\text{min}$  into region where exotherm had started, held at  $80^{\circ}\text{C}$  for ca. 5 min, and cooled at  $10^{\circ}/\text{min}$ ; (b) then reheated at  $20^{\circ}/\text{min}$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

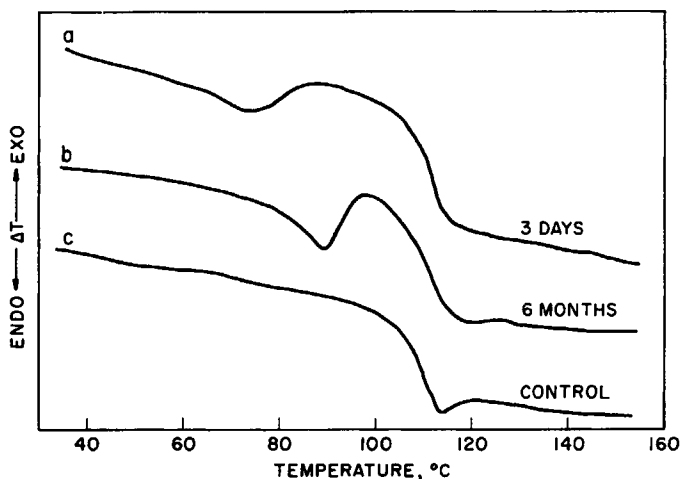


Fig. 10. Differential thermograms of polystyrene vitrified at 3000 atm, taken (a) three days and (b) six months after molding; (c) control. Heating rate here was  $20^{\circ}\text{C}/\text{min}$ .

more difficult to read than the runs at  $10^{\circ}\text{C}/\text{min}$  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

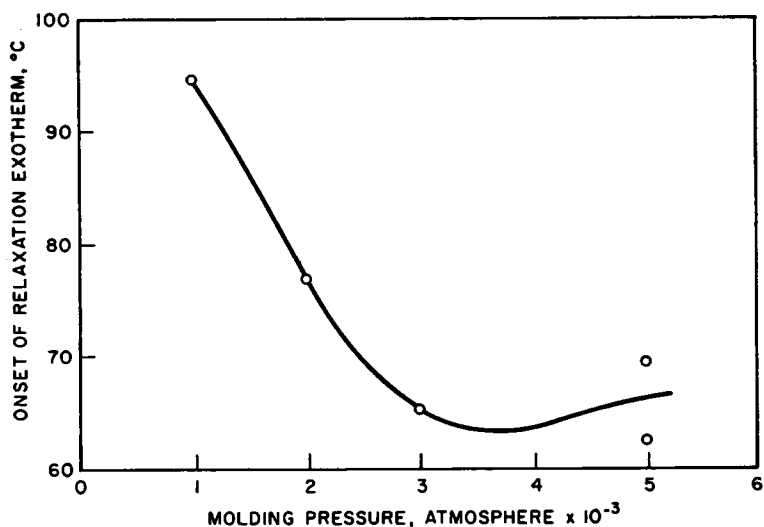


Fig. 11. Effect of vitrification pressure on temperature at which exothermic relaxation first appears in thermogram. Data are for DTA heating rate of  $10^{\circ}\text{C}/\text{min}$  on samples 2-3 days after molding.

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  $T_g$  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

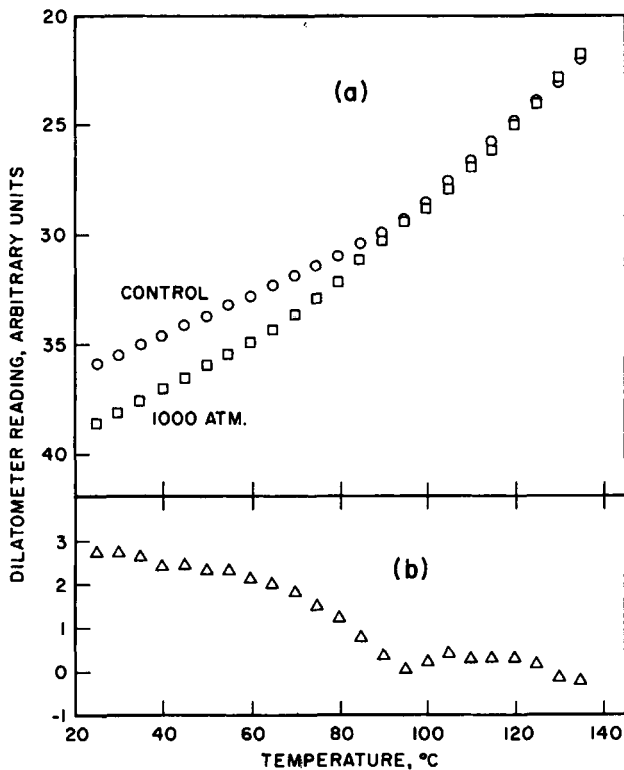


Fig. 12. (a) Dilatometric expansion of ( $\square$ ) polystyrene vitrified at 1000 atm and ( $\circ$ ) reheat control. Heating rate was 0.5°C/min. (b) Volume compaction from difference of curves in (a). One division represents approximately 0.37% difference in volume.

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

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  $0.5^{\circ}\text{C}/\text{min}$ . 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  $80\text{--}90^{\circ}\text{C}$ , 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  $25^{\circ}\text{C}$  and a vapor pressure of 50 mm Hg.

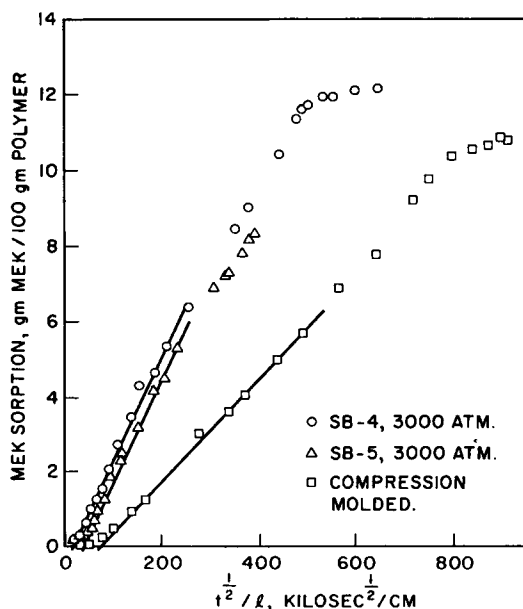


Fig. 13. Sorption of methyl ethyl ketone vapor at  $25^{\circ}\text{C}$  and 50 mm Hg pressure by polystyrene glasses vitrified at (O, $\Delta$ ) 3000 atm and ( $\square$ ) compression-molded control.

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<sup>25</sup> 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,<sup>25–28</sup> 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.<sup>22</sup> 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

molding. At molding pressures above 1000 atm, the number of defects increases again, owing to the formation of high-energy domains consisting of chain conformations which were thermodynamically favorable under the vitrification conditions but are unstable at room conditions. Some of these high-energy structures relax rapidly upon release of the molding pressure to form regions of high local void volume. However, some high-energy structures are constrained by the surrounding compacted polymer matrix and undergo a much slower subsequent relaxation. The decay of such high-energy structural domains is markedly accelerated by heating, straining, or plasticizing the glassy polymer, which results in the faster or greater relaxation phenomena observed in the various methods of testing; i.e., the accelerated decay constitutes an additional relaxation mechanism.

The results suggest that an optimum molding pressure may exist for polystyrene around 1000 atm or somewhat lower. This is not far above the pressures a modern commercial extruder is capable of developing. Below this limit, the effect of higher molding pressure is to reduce the number of microvoid defects and to produce a more compact polymer with stronger interchain cohesion. This is reflected in a higher modulus, higher yield strength, and lower gas permeability.

## CONCLUSIONS

Polystyrene samples molded at pressures in the kilobar range have been found to show (1) a lower mechanical damping factor, due to a loss of independent segmental mobility; (2) higher elastic modulus in simple compression, due to more extensive interchain cohesion; (3) a maximum in compressive yield stress at a molding pressure around 1000 atm; (4) lower strain at yield, which was found to be almost entirely in the "plastic strain" component, and faster relaxation at yield; (5) an exothermic relaxation accompanied by volume dilation, which starts at some temperature below  $T_g$  and continues through the glass transition; and (6) faster relaxation in methyl ethyl ketone vapor, leading to more rapid rates of sorption of vapor.

These results indicate that moderately high molding pressures cause a rearrangement of segmental structure involving compaction of the polymer matrix. This produces samples with higher strength, higher modulus, and lower gas permeability. At higher molding pressures, microstructural defects are generated by the relaxation of high-energy conformations which are unstable at room conditions. The predominance of these defects and high-energy conformations results in a loss of strength and faster relaxation in the presence of solvent, heat, or strain. The existence of an optimum molding pressure for polystyrene is thus indicated to be somewhat below 1000 atm.

The marked improvement in polymer properties resulting from sample preparation using molding pressures greater than those achieved by more conventional molding processes suggest that these higher-pressure molding

procedures may be useful for obtaining polymer materials with modified properties required for more exacting applications. It is anticipated that polymers other than polystyrene, which are more sensitive to pressure compaction,<sup>2,3</sup> may show even greater changes in properties when molded under suitably high pressures.

### References

1. J. M. O'Reilly, in *Modern Aspects of the Vitreous State*, Vol. 3, J. D. Mackenzie, Ed., Butterworths, Washington, 1964, Chap. 3.
2. N. I. Shishkin *Sov. Phys.—Solid State*, **2**, 322, 329 (1960).
3. R. M. Kimmell, Sc.D. Dissertation, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Mass., 1968.
4. S. Saito, *Prog. Polym. Phys. Japan*, **11**, 375 (1968).
5. K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z.*, **183**, 110 (1962).
6. G. Gee, *Polymer*, **7**, 177 (1966).
7. G. Allen, R. C. Ayerst, J. R. Cleveland, G. Gee, and C. Price, *J. Polym. Sci. C*, **No. 23**, 127 (1968).
8. E. Baer, and J. L. Kardos, *J. Polym. Sci. A*, **3**, 2827 (1965).
9. G. Rehage, and H. Breuer, *J. Polym. Sci. C*, **No. 16**, 2299 (1967).
10. C. D. Armeniades, I. Kuriyama, J. M. Roe, and E. Baer, *J. Macromol. Sci. Phys.*, **B1** (4), 777 (1967).
11. S. Matsuoaka, and B. Maxwell, *J. Polym. Sci.*, **32**, 131 (1958).
12. G. Biglione, E. Baer and S. V. Radcliffe, *Fracture 1969* (Proceedings of the 2nd International Conference on Fracture), Chapman and Hall, London, 1969.
13. S. B. Ainbinder, M. G. Laka, and I. Yu. Maiors, *Polym. Mech.*, **1**, 50 (1965).
14. A. Christiansen, S. V. Radcliffe and E. Baer, Proceedings of the International Conference on Yield, Deformation, and Fracture of Polymers, Cambridge, England, March-April, 1970, to be published.
15. W. W. Whitney, Sc.D. Dissertation, Department of Civil Engineering, Massachusetts Institute of Technology, Cambridge, Mass., 1964.
16. W. W. Whitney, and R. D. Andrews, *J. Polym. Sci. C*, **No. 16**, 2981 (1967).
17. R. E. Robertson, *J. Chem. Phys.*, **44** (10), 3950 (1966).
18. R. D. Andrews, S. W. Allison, D. H. Ender, R. M. Kimmell, and W. Whitney, U. S. Army Natick Laboratories, Natick, Mass., 1966, C & OM-25. Also available from Clearinghouse for Federal and Scientific Information as AD-644021.
19. R. D. Andrews and S. W. Allison, *J. Appl. Phys.*, **38** (11), 4164 (1967).
20. M. H. Litt, and P. Koch, *Polymer Letters*, **5**, 251 (1967).
21. R. D. Andrews, *ACS Polymer Preprints*, **10** (2), 1110 (1969).
22. W. C. Dale, M.S. Thesis (C. E. Rogers, Advisor) Case Western Reserve University, Cleveland, Ohio, 1970.
23. B. Wunderlich, and D. M. Bodily, *J. Appl. Phys.*, **35** (1), 103 (1964).
24. G. Moraglio, F. Danusso, U. Bianchi, C. Rossi, A. M. Liqouri, and F. Quadrifoglio, *Polymer*, **4**, 445, 447, 448 (1963).
25. J. Crank, *Mathematics of Diffusion*, Oxford Press, London, 1957.
26. G. S. Park, *J. Polym. Sci.*, **11** (2), 97 (1953).
27. J. Crank, *J. Polym. Sci.*, **11** (2), 151 (1953).
28. J. Crank, and G. S. Park, *Trans. Faraday Soc.*, **47**, 1072 (1951).

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