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, τ, 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.[10] 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

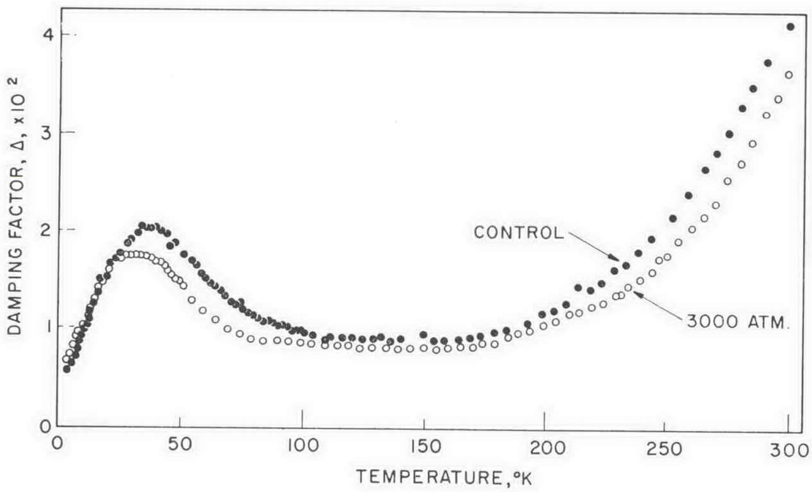

Fig. 1. Cryogenic mechanical relaxation spectrum of polystyrene glasses molded (O) at 3000 atmospheres, and (●) compression-molded control. Torsional pendulum frequency was 1–2 Hz.

dissipates less energy in independent segmental motion. Matsuoka and Maxwell[11] 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 $^1/_4$ 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[a]

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

[a] Results are in the form: mean of five specimens ± one standard deviation.
[b] Greatest (negative) slope after maximum at yield expressed as psi per unit sample strain.