

Mechanical and Relaxation Properties of Polystyrene Molded at High Pressures

W. C. DALE and C. E. ROGERS, *Division of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106*

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.¹ 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 studies²⁻⁷ 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

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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)⁻¹, 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.⁸ 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^{1,5,6,9} 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.⁹

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 3³/₈ 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