ISOTHERMAL ENTHALPY AND DENSITY STUDIES OF POLYMERIC GLASSES VERSUS FORMATION PARAMETERS

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Time-dependent properties of glassy polymers have been studied extensively by observing changes with time of either specific volume or "apparent enthalpy" obtained from scanning-calorimeter-derived specific heats. It is known, however, that the rate of changes of these parameters are dependent not only on temperature but as well on the initial state of the glass;[1] yet few studies have been directed toward systematically correlating more than one processing parameter (commonly, annealing temperature) with more than one ordering parameter. Likewise, little attention has been directed toward the initial state of the glass. In this study we independently control the vitrification pressure (P_v, 15 to 60,000 psi) and vitrification cooling rate (R_v, 0.1° to 400°K/min) and determine enthalpies measured isothermally (Δh_r),[2] densities, and qualitatively compare scanning calorimeter traces. We observe that, for polystyrene at time $= 0$, Δh_r increases linearly and strongly with $\log R_v$ and increases linearly but weakly with P_v. Likewise, we observe that density decreases linearly with $\log R_v$. Most important is the fact that the pressure and cooling rate coefficients of both Δh_r and density are virtually independent, i.e., $\partial \Delta h_r / \partial P_v$ and $\partial \rho / \partial P_v$ are independent of R_v, and $\partial \Delta h_r / \partial R_v$ and $\partial \rho / \partial R_v$ are independent of P_v. Thus we can write:

$$\Delta h_r = \Delta h_{r0} + A \log R_v + B P_v$$

and

$$\rho = \rho_0 + C \log R_v + D f(P_v),$$

where A, B, C, D are constants and $f(P_v)$ is a function of the form $[1 + \exp(-1/P_v)]$. If we eliminate $\log R_v$ from both equations we obtain an expression equating the parameters Δh_r, ρ, and P_v; only two being independent. The uniqueness of this is related to the isothermally obtained enthalpies which are unambiguous in their interpretation. They are of particular value in studying the glassy state because:

1. Enthalpy is a well-defined fundamental thermodynamic parameter.
2. The enthalpies are determined at a constant temperature, important in studying glasses because of the temperature-dependent relaxations.
3. Time can be known exactly up to the start of the measurement.

The method involves techniques of solution calorimetry.[2] This presentation involves only the results at time-0, but relaxation studies are going on. Further, scanning calorimeter traces were obtained on all samples, the results clearly demonstrating that the endotherm superimposed on T_g (which has become associated with enthalpy relaxation) is a strong function of density as well as presumably enthalpy.

REFERENCES

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