# Free-Volume Measurement and Instability in a Sheared Polymer Glass

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Deforming a polymer glass can result in flow, even at temperatures below the glass transition temperature. We show that the local free-volume changes in a sheared glass can be measured using environment-sensitive fluorescence probes dispersed in the polymer matrix. The shear-induced glass transition leads to shear localization for large strains: a region of strongly localized deformation is observed with a large free volume. This transition can be accounted for assuming that the free energy barriers in the glassy free energy landscape decrease strongly with the applied deformation. We reveal the importance of free volume and non-affine contributions to explain the inelastic behavior of a glassy system under large deformation. The Eyring model is only valid at low strain amplitude and fails to explain the yielding behavior at large deformations. We introduce a modified Eyring model to quantitatively describe the mechanical instability and yielding of the material under shear. Furthermore, a microscopic non-affine deformation model is used to quantitatively link the measured free volume changes during the shear-induced glass transition with the observed mechanical instability and with the measured rheology. We provide a deeper understanding of the glass transition, and specifically of the roles of free volume, shear and molecular mobility in the polymer glass transition.

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