Abstract: Semiconducting polymers—typically fabricated as thin films (~100 nm)—have always been associated with flexible applications, such as solar cells, active-matrix displays, and biomedical sensors. Mechanical flexibility of these materials, however, is not automatic. The thermal and mechanical properties of semiconducting polymers must be engineered by tuning the chemical structure, molecular weight, processing conditions, and interactions with other materials in the device stack. The thermal transition of semiconducting polymers that perhaps most greatly influences the mechanical response is the glass transition, and the temperature ($T_g$) at which it occurs. We develop a new technique that leverages the unique aggregation behavior of semiconducting polymers to measure the $T_g$. With ultraviolet–visible (UV–vis) spectroscopy, we measure changes in the absorption spectrum due to rearrangement of chains at the molecular scale and formation of photophysical aggregates on heating above the $T_g$. Thermal transitions are not the only properties of semiconducting polymers that are challenging to measure; the mechanical properties, too, of these materials are difficult to characterize due to the diverse range of fracture behavior that thin polymer films exhibit. In addition, the mechanics that govern ductile fracture—compared to brittle fracture—are underexplored. Understanding the mechanics of ductile fracture is crucial for the improved design and fabrication of mechanically robust organic electronics. For this mechanism of fracture, we find that diamond-shaped microvoids, which originate at pinholes and defects within the film, propagate with an aspect ratio that increases linearly with applied strain. We define the rate of change of the aspect ratio of a microvoid with respect to applied strain as the “microvoid-propagation number.” This dimensionless film parameter, previously unreported, is a useful measure of ductility in thin films supported by an elastomer.

Image 1. Convenient approaches for quantifying the fracture behavior of both brittle and ductile thin films of semiconducting polymers.

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