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Calorimetric Tg and Heat Capacity of Polystyrene Thin Films[1]
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The glass transition temperature and the absolute heat capacity of polystyrene thin films were measured using the step-scan method of differential scanning calorimetry. The glass transition temperature is found to be depressed 8 K for a sample of stacked 17 nm thick films and Tg is depressed 3 K for a sample of stacked 61 nm thick films. The results are consistent with data in the literature for the Tg depression in supported polystyrene films although our films are expected to be "freely standing" for the initial DSC scan. In addition, the absolute heat capacity in both the liquid and glassy states decreases with decreasing film thickness, the step change in heat capacity at the glass transition temperature decreases with decreasing film thickness, and the breadth of the transition region increases with decreasing film thickness. The effect of heating the thin film samples to 135 $^{\circ}$C, approximately 40 $^{\circ}$C above their Tgs, is a slight increase in the absolute heat capacity and a slight increase in Tg. No significant changes occur on subsequent scans. The "thin film" morphology is maintained in spite of scanning to above Tg where the stacked film sample is expected to lose its free surface.

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