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β-NMR Studies of the Temperature and Depth Dependence of Dynamics in Polystyrene Thin Films

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The decrease of the glass transition in polystyrene thin films with decreasing film thickness has given rise to the suggestion that there is a region near the free surface where there are faster dynamics than in the bulk. This surface mobility has been directly measured, but there are few studies of how the enhanced dynamics varies with distance from the free surface. We have used β-detected nuclear magnetic resonance (β-NMR) of implanted $^{8}Li^{+}$ to directly probe the temperature and depth dependence of the γ-relaxation mode, which is due to phenyl rings undergoing restricted rotation, in thin films of atactic deuterated polystyrene (PS-d8). I will show that the activation energy for the γ-relaxation is lower near the free surface and returns to bulk values at depths of $\sim$10 nm and discuss how the depth dependence of γ-relaxation is affected by sample processing (such as annealing, floating on water and the inclusion of a surfactant), and by the presence of a buried interface. I will introduce a novel hole-burning (selective saturation) β-NMR technique that has been used to measure the depth dependence of the fluctuation rate of a much slower relaxation process.

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