

# 15th International Conference on Muon Spin Rotation, Relaxation and Resonance



Contribution ID: 158 Contribution code: P-MON-13

Type: Poster

## $\beta$ -NMR studies of the temperature, depth and molecular weight dependence of dynamics in normal and ultrastable polystyrene glasses

Monday, 29 August 2022 18:40 (20 minutes)

The observation that the glass transition temperature of polystyrene (PS) thin films decreases with decreasing film thickness led to the suggestion that there is a very thin layer near the free surface where the polymer motion is faster than in the bulk. Direct confirmation of enhanced dynamics near the free surface has proved elusive as few techniques can measure how the dynamics varies with distance from the free surface on the nm length scale and those that can either use bulky probes or multilayer films that modify the dynamic gradients. Implanted  $^8\text{Li}^+$  is a much less perturbing probe and with  $\beta$ -detected nuclear magnetic resonance ( $\beta$ -NMR) we can measure the depth dependence of the  $\gamma$  relaxation of PS, which involves motion of the phenyl side groups.<sup>1,2,3</sup> The  $\gamma$  relaxation has a double exponential depth dependence from the free surface, with a characteristic length of  $\sim 6$  nm. We have produced ultrastable glass (USG) films of low-molecular weight PS by physical vapor deposition that exhibit properties similar to those of a normal glass (NG) that has been aged for several years. Our  $\beta$ -NMR measurements indicate the bulk  $\gamma$  relaxation is slower in the USG compared with the NG while the opposite is true near the free surface where the  $\gamma$  relaxation is faster in the USG compared with the NG. These trends are more significant for samples with a larger apparent age.

1. I. McKenzie et al., *Soft Matter* **2015**, *11*, 175
2. I. McKenzie et al., *Soft Matter* **2018**, *14*, 7324
3. I. McKenzie et al., *J. Chem. Phys.* **2022**, *156*, 084903

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**Session Classification:** Posters

**Track Classification:** Molecular chemistry and chemical physics