Depth-resolved Glass Transition below the Free Surface of a Polymer

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Intensive studies of polymer films have followed the discovery of significant suppression of the glass transition temperature T_g for freestanding films of nanoscale thickness [1]. A local T_g that depends on distance from a free surface has often been invoked to explain these results, but there has previously been a lack of experimental techniques able to resolve directly such dependence in an individual sample. Here we demonstrate how low energy muons (LEM) can be used to make depth resolved measurements of the local T_g near the surface of a polymer film, which can be used to identify the mechanisms responsible for the local reduction of T_g. Measurements have recently been obtained for polybutadiene (PB) and previously for polystyrene (PS) [2]. These results are compared and a consistent picture emerges in which a kink diffusion mechanism first proposed by de Gennes [3] operates over a length scale determined by the size of the polymer chain, crossing over at longer distances to a capillary wave mechanism first proposed by Herminghaus [4].

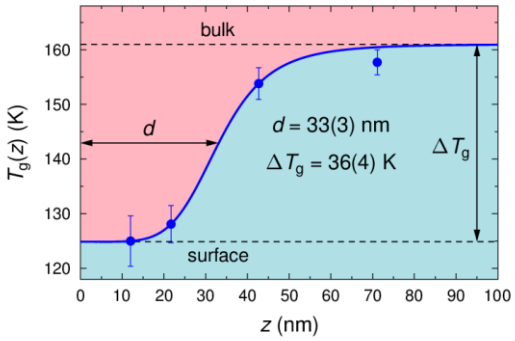

Fig. 1 LEM-measured local T_g near the free surface of a polybutadiene film.

References

[1] J.L. Keddie, R.A.L Jones and R.A. Cory, Europhys. Lett. **27**, 59 (1994).
[2] F.L. Pratt et al, Phys. Rev. B **72**, 121401(R) (2005).
[3] P.G. de Gennes, Eur. Phys. J. E **2**, 201 (2000).
[4] S. Herminghaus, Eur. Phys. J. E **8**, 237 (2002).