O JMC15

**Modification of the bulk chain conformation in ultra-thin polymer films observed by Small Angle Neutron Scattering**

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The stability of thin polymer films on solid substrates has attracted significant interest to fundamental studies on the molecular processes and the physics that govern the behavior of polymer chains under confinement. In particular, deviations of the glass transition temperature, Tg, from bulk values observed in ultra-thin films led to numerous works on polymer dynamics. For **polystyrene (PS), the Tg value decreases with decreasing film thickness h, for h<50nm**.1 In order to explain this phenomenon, the possible presence of a surface polymer layer with higher mobility than in the bulk, and the reduction of the diffusion coefficient of polymer chains due to chain adsorption on the substrate with opposite effect were widely debated. Some questions about conformation and chain entanglement were also raised. Small Angle Neutron Scattering (SANS) is the only technique that allows direct measurement of the chain conformation in bulk by using blends of deuterated and hydrogenated chains. However, such measurements are rare and difficult because of the very small amount of sample volume and of many effects like dewetting or presence of remaining solvent that can lead to erroneous conclusions.

We have first compared the local chain conformation of PS in films of **10nm and 100nm thickness**. We concluded to an increase of the persistence length lp from ~22Å to ~ 40Å for 100nm and 10nm films respectively2, thus much larger than 9.2Å, the bulk value. These measurements were in contradiction with the ones of Jones et al.3, who claimed the absence of deviation from the gaussian bulk conformation for thin PS films. Recently, we have measured a series of **15nm thickness** films ofmolecular weight ranging from 70K to 1500K, thus - in principle - increasing confinement ratio (h/Rg bulk). At low Q, Q.Rg<1, no important change compared to the bulk behavior is measured, as already concluded by Jones et al.3 At high Q, the scattering curves show significant deviation from bulk’s curve, confirming our previous results2. Since no influence of the confinement ratio h/Rg is observed, we now conclude that the modification of the local chain structure observed is not an effect of chain confinement but another effect not present in bulk and hence visible only at low film thickness. These results and their possible origins will be presented.

1. Forrest et al. Phys. Rev. Lett. 77, 2002,1996. Keddie et al. Europhys. Lett. 27, 59,1994.
2. Brûlet et al. Macromolecules 33, 997, 2000.
3. Jones et al. Nature 400, 146-149, 1999.

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