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Tuning the Tg-Confinement Effect by Controlling the Amount of Residual Surfactant Present in Emulsion Polymerized Polystyrene Thin Films LAWRENCE CHEN, JOHN TORKELSON, Northwestern University — The nanoconfinement effect of polystyrene (PS) ultra-thin films supported on silica has been well studied over the past two decades. In order to systematically study the influence surfactants have on the Tg-confinement effect in thin films, PS was synthesized using conventional emulsion polymerization (E-PS) using sodium dodecyl sulfate (SDS) as the surfactant. After rigorous purification, the amount of SDS remaining in the bulk E-PS sample was quantified by using a modified Epton's Method to be 0.023 wt%. This technique not only allows us to quantitate the amount of surfactant present in bulk polymer but also allows for the fine-tuning of surfactants present in the polymer. We find that a minute amount of surfactant is capable of significantly suppressing the Tg-confinement effect as well as narrowing the Tg breadth in sufficiently thin E-PS films; the magnitude of the Tg-confinement effect is strongly dependent on the amount of SDS present in bulk E-PS. Finally, using XPS depth profiling we demonstrate that the anionic surfactant preferentially resides at the free surface layer of the film thus eliminating the free surface effect.

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