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A new approach to study of the onsets of tethered chain overcrowding and highly stretched brush regime utilizing crystalline-amorphous diblock copolymers

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Two series of diblock copolymers, PEO-*b*-PS and PLLA-*b*-PS, were used as templates to generate tethered PS blocks on the single crystal surfaces. Controlled and tunable reduced tethering density, $\tilde{\sigma}$, defined by $\sigma \quad \pi \ R_g^2$ (where σ is the tethered chain density), could be achieved in a broad range (up to 24) by changing the molecular weights (MW's) of the crystalline and amorphous blocks and by varying the crystallization temperature (T_x) of different PEO-*b*-PS and PLLA-*b*-PS solutions. The $\tilde{\sigma}$ of the tethered PS chains on the crystal surface increased with increasing T_x because at a fixed MW of the PEO or PLLA block, an increase in the lamellar thickness (d_{CRYST}) was evidence of a decrease in the number of folds. When we plotted the relationships between $1/d_{CRYST}$ and T_x for these two series of diblock copolymers, sudden and discontinuous changes of the slopes in some of these were observed at $\tilde{\sigma} = 3.7$ ($\tilde{\sigma}$*). This was as a result of the drastic interaction change of the neighboring PS tethered chains. An average reduced surface free energy of the tethered PS chains (Γ^{PS}) was used as a parameter to characterize the PS tethered chain interactions. The relationship between Γ^{PS} and $\tilde{\sigma}$ showed a discontinuous transition at $\tilde{\sigma}$*. This could be identified as the onset of the tethered PS chain overcrowding in solution. This transition indicates that the extra entropic surface free energy created by the repulsion of tethered PS chains started to affect the nucleation barrier of the PEO or PLLA block crystallization. Based on the scaling laws, the onset of highly stretched brush regime could be identified at $\tilde{\sigma} = 14.3$ ($\tilde{\sigma}$**). In the Γ^{PS} versus $\tilde{\sigma}$ plot, the transition appears to be continuous. Thus, a crossover regime in the tethered PS chains exists between $\tilde{\sigma}* = 3.7$ and $\tilde{\sigma}^{*}* = 14.3$. It is defined as the regime where the interaction of the tethered PS chains undergo changes from being non-interacting towards penetration to, finally, chain stretching normal to the surface.