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### **Crystallization and Phase Transitions in Polymer Nanolayered Systems under Confinement<sup>1</sup>**

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Forced assembly multiplication coextrusion has been reported as an advanced technique to study crystallization and phase transitions for polymers under confinement. This technique can readily produce continuous alternating layered structures composed of two or three polymers [1, 2]. Multilayer films fabricated by multiplication coextrusion consist of hundreds or thousands of layers with individual layer thickness varying from 10 nanometers to several micrometers. The flexibility of this novel multiplication coextrusion process, particularly at the nanoscale, enables the study of confinement effects on polymer crystallization and phase transitions. We have discovered that the hierarchical morphology of many polymers can be manipulated by confinement between rigid layers [2]. Spherulites are flattened and lamella single crystals are oriented as the confining scale is decreased towards the nano-level. Poly(ethylene oxide) (PEO), poly( $\epsilon$ -caprolactone) (PCL), syndiotactic polypropylene (sPP) and poly(vinylidene fluoride) (PVDF) will be given as unique examples of this phenomena [2, 3]. Depending on the crystallization temperature, two major lamellae orientations “in-plane” or “on-edge” can be achieved, which dramatically affect the multilayer film characteristics, such as film barrier properties [2, 4]. For some polymers such as high density polyethylene (HDPE), in-plane lamellae orientation is difficult to achieve. However, at the micro-scale, confined HDPE spherulites have tilted lamellae, which also improve gas barrier properties. Nanoscale multilayer films were also utilized to produce submicron size polymer droplets by thermal breakup of the layers [4]. Phase transitional behaviors during fractionated crystallization of these droplets will be described as a powerful tool for the study of both heterogeneous and homogeneous nucleation.

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