Block polymers (BPs) have attracted significant attention for emerging nanotechnologies such as nanolithographic masks, nanotemplates, nanoporous membranes, organic photovoltaics, and lithium ion battery membranes due to their ability to self-assemble into periodic assemblies of nanoscale features. Many of these applications require thin film geometries, which have additional confinement interactions in comparison to bulk self-assembly that must be understood to control nanostructure orientation, ordering, and alignment precisely. Two approaches to study the nuanced effects of these additional interactions are in situ characterization and neutron scattering, used concurrently or independently. With these techniques, more predictive and optimized methods to direct self-assembly can be established to unlock the full potential of BP thin films in commercial and research applications. In this dissertation work, four aspects of BP thin film self-assembly were explored with these powerful characterization tools. First, chlorosilane-modified substrate surfaces were employed to investigate the effect of the substrate-polymer interaction on nanostructure orientation and ordering. Predictive formalisms were developed that defined substrate wetting behavior, nanostructure ordering, and through-film orientation control as a function of total and decoupled (dispersive and polar) substrate-polymer interfacial energy components. Second, solvent vapor annealing was studied with in situ small-angle neutron scattering (SANS), neutron reflectometry (NR), and selective deuteriation to determine how factors such as solvent-polymer interactions and solvent concentration affected BP thin film self-assembly. Next, in situ SANS during solvent vapor annealing with soft shear (SVA-SS) was used to track shear-induced nanostructure disordering and ordering. By understanding the kinetic pathways during SVA-SS, more robust and high-throughput methods to define the alignment direction(s) were developed. Lastly, lithium salt-doped poly(styrene-b-oligo[oxyethylene] methacrylate) films were investigated with NR to achieve the first high-resolution, non-destructive, and quantitative analysis regarding how lithium salts distribute within the conducting domain of BP electrolyte thin films. Overall, the work in this dissertation contributes predictive and translatable approaches to direct self-assembly and the design of powerful characterization strategies to extract key information from BP thin film systems to improve their rational design and application.