The ability of block copolymers to self-assemble into highly organized nanostructures is well established. Although simple “AB” diblocks have been studied extensively, and the rules governing the selection of morphology almost quantitatively established, this architecture is inadequate for many applications. For example, the most commercially successful block polymers to date are thermoplastic elastomers produced from ABA triblocks, in which the formation of a network structure (“A” crosslinks in a “B” matrix) confers substantial mechanical strength. Indeed, a simple argument based on chain bridging suggests that at least four blocks (ABAB…) are necessary to secure optimum toughness. Similarly, the desire to incorporate multiple functionalities into self-assembled materials has initiated extensive experimental explorations of ABC triblock terpolymers, as well as even more elaborate architectures. Significant advances in controlled polymerization technique have enabled preparation of almost any conceivable block polymer architecture. However, this synthetic flexibility immediately poses two questions: how does one decide what architecture to make, and how does one accurately characterize the material that has been made? In this talk examples of interesting multiblock architectures will be provided, and issues surrounding their characterization will be identified.