At large length-scales, the architecture of polymers can be described by a coarse-grained specification of the distribution of branch points and monomer types within a molecule. This includes molecular topology (e.g., cyclic or branched) as well as distances between branch points or chain ends. Design of large length-scale molecular architecture is appealing because it offers a universal strategy, independent of monomer chemistry, to tune properties. Non-linear analogs of linear chains differ in molecular-scale properties, such as mobility, entanglements, and surface segregation in blends that are well-known to impact rheological, dynamical, thermodynamic and surface properties including adhesion and wetting. We have used Self-Consistent Field (SCF) theories to describe a number of phenomena associated with large length-scale polymer architecture. We have predicted the surface composition profiles of non-linear chains in blends with linear chains. These predictions are in good agreement with experimental results, including from neutron scattering, on a range of well-controlled branched (star, pom-pom and end-branched) and cyclic polymer architectures. Moreover, the theory allows explanation of the segregation and conformations of branched polymers in terms of effective surface potentials acting on the end and branch groups. However, for cyclic chains, which have no end or junction points, a qualitatively different topological mechanism based on conformational entropy drives cyclic chains to a surface, consistent with recent neutron reflectivity experiments. We have also used SCF theory to calculate intramolecular and intermolecular correlations for polymer chains in the bulk, dilute solution, and trapped at a liquid-liquid interface. Predictions of chain swelling in dilute star polymer solutions compare favorably with existing PRISM theory and swelling at an interface helps explain recent measurements of chain mobility at an oil-water interface.

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1This work was supported by NSF Grants No. CBET- 0730692 and No. CBET-0731319.