

### *Polymer Thermodynamics and Chain Structure*

Polymers display some similarities and some differences with nano-aggregates. Both materials are composed of basic units, Kuhn units for polymers which are rod-like molecular to nano-scale and regular structures and primary particles of nano-aggregates which are typically nano-scale irregular crystals, crystallites or amorphous particles. In both cases the substructure joins in a close to topologically linear fashion to form a convoluted chain structure called an aggregate in nanomaterials and a polymer coil in Polymer Science. The mass-fractal or minimum dimension of a polymer chain is determined by thermal equilibrium due to flexible covalent bonds between Kuhn units and the generally molecular size of the regular units. For ceramic aggregates, multiple ionic bonds between primary particles typically make the structure effectively rigid and not subject to thermal equilibrium. The mass fractal dimension or minimum dimension (for branched aggregates) is determined kinetically during formation and growth of the aggregates. For both ceramic aggregates and polymer coils the branch content and connectivity dimension,  $c$ , are determined by formation/reaction kinetics and transport features during growth.

The flexibility of polymer coils allows significant overlap between coils when concentrations are greater than that of average overlap,  $c^*$ . This allows for entanglement of chains which influences the mobility of individual chains and has dramatic effects on both the rheology and processing of polymeric fluids which are highly non-Newtonian, as well as the mechanical properties of solid plastic parts which display distinctive non-Hookean behavior. Ceramic aggregates with mass-fractal dimensions near 2 or higher can not significantly overlap or entangle. The mechanical response of an individual polymer coil and a ceramic aggregate show some similarities and striking differences as recently shown by Friedlander at UCLA. Both structures display a spring like behavior when subjected to tensile strain, for instance, that reduces in spring constant with mass of the structure as shown theoretically by Witten at the University of Chicago for aggregates and by the late Paul Flory of Stanford for polymer coils. Since the spring constant of a polymer coil is related to conformational changes that occur with tension, and because the conformation of a polymer coil is largely determined by entropy, an individual polymer coil displays an increasing spring constant with increasing temperature in direct analogy to the increased pressure of an ideal gas with temperature. Ceramic aggregates show a weak temperature dependence with lowered modulus with higher temperature.

A major difference between polymer coils and ceramic aggregates is the "adaptability" of a polymer coil to external and internal forces. Adaptability for a polymer coil at thermal equilibrium means that the uniform mass-size scaling observed for dilute coils in very good solvents breaks up into two or more regimes of mass-size scaling to accommodate changes in thermodynamics at different size scales in different ways so that the total Gibbs free energy for the hierarchical structure is minimized. Though the concept of hierarchical structures in thermodynamic equilibrium in polymers was first developed in the late 1970's by deGennes and Edwards, the implications in terms of a structural model based on thermodynamics and as a tool for predicting properties is still in its early stages. In a recent paper by UC researchers, this concept was applied to equilibrium swollen networks (rubbers swollen in a good solvent). An elastomer is a polymer which would normally be a liquid with chains chemically bonded together in a network to form a solid structure. When an elastomer is placed in what

would normally be a solvent for the base polymer chains it swells to a fixed size while retaining solid features. Such gels are used in disposable diapers by P&G to absorb body fluids for instance. The chains in the network prior to swelling display a Brownian walk structure,  $d_f = 2$ , that would uniformly decrease to  $5/3$  if the chains were not crosslinked. For model end-linked elastomers UC researchers have performed neutron scattering studies at Argonne National Laboratories as well as at NIST that indicate a hierarchical structure on swelling that differs dramatically from the chain conformation expected from conventional models for swollen elastomers. UC has contributed a new model for this observed hierarchical structure based on work of Pincus (UCSB) and Witten (UChicago). The theory is based on a simple concept, that larger chain structures, having a lower modulus, can deform more easily and will deform first leading to two regimes of structural scaling on swelling. Such a hierarchical structure can be demonstrated with a string on an overhead projector or on a table. If the string is drawn from the two ends, the original randomly coiled conformation is deformed, but not uniformly at all size scales. That is the smallest kinks in the string straighten last since the larger lever arm on the large size scales results in a larger straightening force. In polymers where the coiling is enforced by entropic considerations a size scale where this force becomes larger than the entropic retracting force can be determined and a scaling transition size can be calculated from first principles. This model agrees with measurements on swollen elastomers and is consistent with the observed mechanical properties.

UC workers have also addressed issues related to the base Kuhn unit of polymer coils in neutron scattering measurements, partly in collaboration with P&G's Miami Valley Laboratory as well as with workers at Argonne National Laboratory. This work is not yet published but examines thermal changes in Kuhn length and the implications on miscibility. Another study done at UC has examined large scale structures observed in polymer solutions using ultra-small angle x-ray scattering at UNICAT, Advanced Photon Source, Argonne National Laboratories. In addition to these areas, Amit Kulkarni (graduate student) is studying miscibility controlled by chain branching and new methods to determine chain branching, especially as regards polyolefins with partial support of Equistar Chemical in Cincinnati, which is the largest manufacturer of polyethylene in the US.