

One-, Two-, and Three-dimensional Superstructured Materials from Well-defined, Complex Nanoscale Components

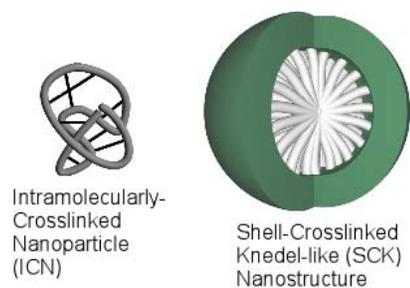
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This Nanoscale Interdisciplinary Research Team is composed of researchers from five institutions with expertise in chemistry, engineering, materials science, and earth and planetary sciences, focused upon the central objectives that include the development of synthetic strategies and characterization protocols for the production and study of one-, two- and three-dimensional superstructures comprised of stabilized nanoparticle assemblies.^[1] The synthetic approach involves the systematic ordering, in solution, upon substrates, and via co-crystallization with inorganic salts, of complex nanoscale components (CNCs) that are either intramolecularly-crosslinked polymer chains^[2] or intermolecularly-shell crosslinked polymer assemblies,^[3] to create composite morphologies that are not accessible in the phase diagrams of the copolymers directly. Physical and chemical manipulation of the CNCs, which are produced via covalent stabilization (crosslinking) of supramolecular assemblies (collapsed single polymer chain or solution-state assemblies of block copolymers), has been shown to produce discrete nanostructures that are also not accessible through self assembly alone.^[4] Moreover, much effort is directed toward investigation of the phase diagrams of block copolymers in solution combined with their intermolecular crosslinking to produce robust CNCs having tunable sizes and shapes.^[5] This team brings strength in a diverse range of tools to study the nanoscopically-resolved complex materials and their one-, two- and three-dimensional superstructures.

Fundamental studies of the structure and properties of the intramolecular- and shell-crosslinked nanoparticles have utilized spectroscopic (solid-state NMR, Raman spectroscopy), scattering (dynamic light scattering, SANS), microscopy (TEM, SEM, confocal fluorescence microscopy), and rheological tools. Rheological studies revealed that addition of the intramolecularly-crosslinked nanoparticles (ICNs) to a polymeric liquid produces a viscosity decrease at odds with Einstein's century-old prediction of the viscosity increase that *Brownian* particles provide.^[6] Organic nanoparticles, synthesized by intramolecular crosslinking of single polystyrene chains, were blended with linear polystyrene macromolecules to produce the viscosity decrease. High crosslink density within the collapsed macromolecules created shape persistent nanoparticles, as was determined by SANS (Figure 1). Significantly, it was found that when the collapsed polystyrene was blended with linear polymer, well-dispersed composites were produced up to 0.5 mass fraction. At this concentration, the interparticle separation is *ca.* 1 nm and is much



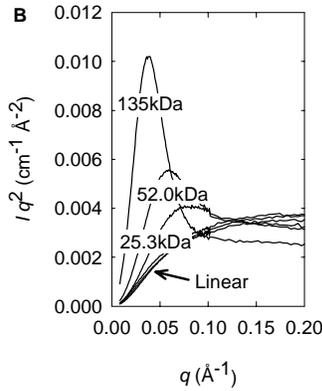


Figure 1. Kratky plot of SANS spectrum for tightly crosslinked nanoparticles compared to starting linear polymers.

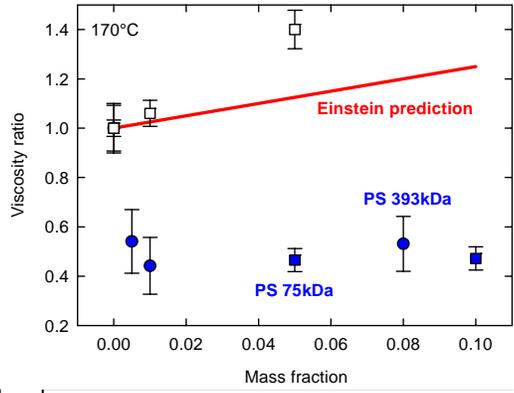


Figure 2. Graph showing how the viscosity changes with nanoparticle concentration (filled symbols) vs. micron-sized particles (open symbols) and Einstein's prediction.

smaller than the linear polymer radius of gyration (≈ 10 nm), allowing polymer distortion without the usual flocculation seen in larger particle systems under similar conditions. The glass transition temperature was also found to decrease under these conditions, which may also contribute to the viscosity decrease (Figure 2).

Consequently, Einstein is not incorrect, rather the polymeric liquid's properties change when nanoparticles are added introducing new physics not included in the original theory. The exact mechanism is unknown at this point, and remains a challenge for theoreticians, but the observation does add further evidence to the unique effects that nanoscale materials can have on bulk physical properties. This research could be useful in a variety of applications ranging from enhanced polymer processing strategies to improved thin film fabrication techniques for microelectronic devices.

In addition to the preparation and study of the CNCs, assembled in ordered arrays in neat form upon substrates and patterned substrates, their co-crystallization with inorganic salts is being pursued. Shell crosslinked (SCK) nanoparticles have demonstrated co-crystallization with NaCl, and this process has been studied in further detail, by atomic force microscopy, confocal fluorescence microscopy, Raman spectroscopy and FESEM. Because the surface chemistry of the SCKs can be controlled accurately, their electrostatic interactions with themselves and substrates can be controlled. However, it was also observed that the SCKs underwent interesting co-crystallization with inorganic salts (NaCl, KCl, etc.), as observed for microcrystals by atomic force microscopy (Figure 3(a)). Macroscopic crystals were observed to contain opaque central regions, for example as is shown in the image (Figure 3(b)) below.

These macroscopic crystals will be of significant interest, as well-defined and ordered organic-inorganic nanocomposites, if it can be determined that the nanoscale ordering of AFM image (a) translates/continues

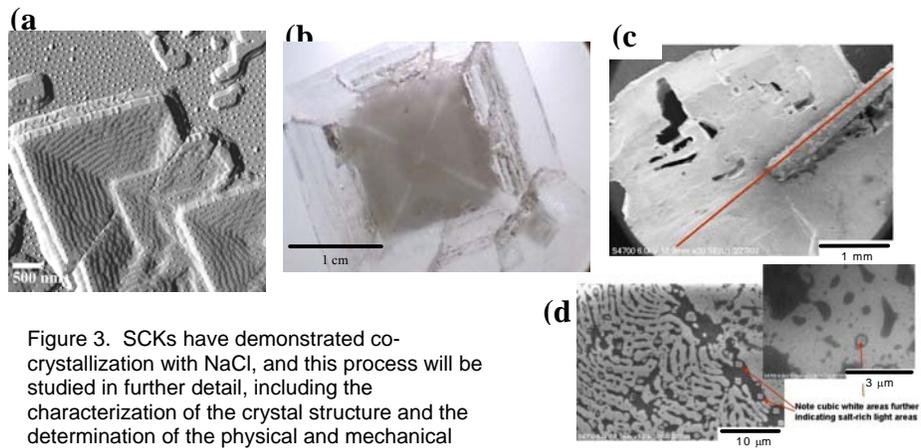


Figure 3. SCKs have demonstrated co-crystallization with NaCl, and this process will be studied in further detail, including the characterization of the crystal structure and the determination of the physical and mechanical properties

throughout the macroscale crystals (b). The diverse team members of this NIRT grant have applied a number of techniques toward the characterization of several (co)crystals of inorganic salts grown in the presence of SCK nanoparticles. Most notably, optical microscopy has revealed rectangular fluid inclusions throughout the central cloudy regions of the crystals, but no distinguishing features within the outer transparent regions. The nanoscale (10-100 nm) diameters of the SCKs prevent their visualization optically using light of visible wavelengths. However, FESEM has revealed contrast that is not related to topographic features, but rather heterogeneous elemental distributions resulting from backscattered electrons from higher atomic number species (Na and Cl) vs. the C, H, N and O of the SCKs. As is shown in image (d) below, collected by FESEM in the transparent region that is noted below the red line of image (c), inferred SCK-rich (dark) regions are phase segregated from SCK-poor (light) regions. Further characterization is in progress. These materials are expected to possess interesting physical and mechanical properties, as are often observed for inorganic nanocrystalline materials found in nature.^[7]

Our team has placed emphasis upon education and outreach activities. In addition to several school visits in each of the five cities (Saint Louis, MO, San Jose, CA, Pittsburgh, PA, Lansing, MI, Newark, DE), a full semester hands-on outreach course has been team taught to K-8 teachers in Saint Louis, with modules being taught by Pasteris, Hawker, Schaefer (see image to the right) and Wooley. Several team exchanges have taken place, with students and postdoctoral associates working for several week stays at various team sites, which has greatly impacted the research productivity, enhanced technology transfer among the sites, and broadened the team members' education and expertise.



References

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