

Self-assembled, nano-structured 3-d polymer spheres: synthesis and chemical characterization by scanning transmission X-ray microscopy

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Nano-structured polymer systems are of interest for a wide range of applications, including 2-d and 3-d optics, separation science applications, catalysis, adhesives, coatings, chemical delivery, etc.[1] Improved performance can often be achieved by controlling the internal chemical composition, for example, to regulate rates and circumstances of release by modifying the trans-wall diffusion of chemicals contained within the interior of a structure. Using timed addition of reagents during microsphere growth we are developing new methods to assemble novel, multi-layer, onion-like particles. Submerged shells may ultimately contain agents for controlled release, catalysts separated by shells of controlled porosity, or high refractive index materials. Optimizing both synthesis and ultimate function requires accurate quantitative chemical analysis of the polymer structure at a spatial resolution that is better than the 50-200 nm scale of the internal structures. Soft X-ray spectromicroscopy, also known as NEXAFS microscopy, is a powerful tool for quantitative chemical analysis, with state-of-the-art spatial resolution of 25 nm. Due to its high chemical sensitivity, ability to penetrate water, and lower radiation damage than electron beam techniques, the scanning transmission X-ray microscopy (STXM) variant is an ideal tool to study soft matter such as polymeric, biological, and environmental systems [2,3]. In recent years we have combined STXM and polymer synthesis to explore core-shell systems, gradients in capsule walls, sphere-capsule assemblies and PS/PMMA blend onions – see [2,3] for examples and references.

Here we report on recent studies of phenylmaleimide (PMI)-rich layers introduced by timed addition of co-monomer during precipitation polymerization of divinylbenzene (DVB). Fig. 1 outlines the synthetic scheme while Fig. 2 presents SEM and TEM images. In order to properly understand and optimize these internal structures we have used C 1s STXM image sequences to generate quantitative chemical maps of microtomed sections of the onion-like spheres. Fig. 3 presents derived chemical maps for a two layer structure. Similar results have been obtained for 1, 2, 3 and 4-layer structures. Detailed, radially averaged line profiles of the composition, as presented in Fig. 4, provide the basis for exploring detailed models of the competition between reaction kinetics, diffusion and interface chemistry that are involved in establishing the structure. Through these studies we expect to develop sharper interfaces, narrower structures, and also to evolve to multiple layered structures with different chemical species in each layer. Such structures are sought as a means of implementing in polymer systems, highly wavelength selective diffractive optics that might be of use in optical communications, optical computing and advanced coatings.

References

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