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Diffuse Polymer Interfaces in Lobed Nanoemulsions Preserved in Aqueous Media

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Two-phase polymeric nanoparticles can place thermodynamically incompatible materials with widely dissimilar properties in intimate proximity to each other. Because their surface properties can vary dramatically over nanolength scales, this class of nanoparticle is attractive for emerging applications in directed self-assembly,[1,2] and their high surface-to-volume ratio together with the fact that hard and soft phases can be mixed at nanolength scales renders them useful for advanced coatings, textiles, pigments, and personal-care applications. One important synthetic route to create these materials polymerizes monomeric precursor dissolved in a parent emulsion polymer so that the growing incompatibility drives nanoscale phase separation.[3−6] At the end of the process, one phase often partially engulfs the other phase, and these structures have been referred to as acorn emulsions or lobed structures because of this morphology.

We have synthesized lobed-type nanoparticles by emulsion polymerization of methyl acrylate (MA), methyl methacrylate (MMA), and vinyl acetate (VA) dissolved in seed latex particles of polydimethyl siloxane (PDMS) suspended in water. The weight ratio of PDMS to the monomers was approximately 1. The molecular weight (M_w) of the PDMS seed emulsion was 25 kg/mol, and after polymerization, the M_w of the organic copolymer was 1400 kg/mol. GC analysis shows less than 5 ppm of residual monomer in the final emulsion. Ultrathin films were created by immersing holey-carbon TEM grids in the emulsion solution. Excess water was removed, and the grids were then plunged into liquid propane. Specimens were cryo-transferred to a 200 keV field-emission scanning transmission electron microscope (STEM) and imaged at −165 °C.

High-angle annular-dark-field (HAADF) STEM imaging (Figure 1) shows that lobed-type emulsions are formed by the copolymerization of MA, MMA, and VA monomers in a PDMS seed emulsion. The two-phase morphology is consistent with theoretical predictions based on the distribution of spreading coefficients.[3−6] Because PDMS preferentially scatters electrons to high angles, the PDMS-rich phase has bright contrast in a HAADF STEM image, while the darker contrast represents the copolymer-rich phase. Profiling across the interface between the two lobes in these images indicates that the transition from light to dark contrast occurs over approximately 10 nm. However, HAADF STEM image contrast does not provide quantitative compositional information, and the heteropolymer interface remains inadequately characterized by this approach.

The nature of the heteropolymer interface within an individual lobed nanoemulsion particle is particularly significant because it can determine many important properties. At one extreme, the interface can be sharp with a compositional variation across it defined by a balance of entropic and enthalpic contributions.[7−9] In this case, the interfacial strength would be relatively low. However, kinetic effects due to the increasing molecular weight of the product polymer can prevent the system from achieving this equilibrium interfacial width.[10,11] Such an interface can be much larger than predicted thermodynamically, and the added strength brought by a diffuse interface will resist separation when subjected to applied loads during subsequent handling.[12]

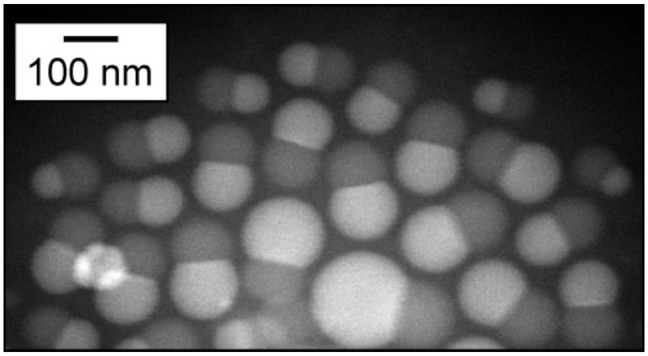

Figure 1. HAADF cryo-STEM image of copolymer (dark contrast), PDMS (light contrast) acorn emulsion structures embedded in amorphous ice (continuous darkest contrast).

Commonly used characterization techniques, such as SEM, TEM, AFM, NMR, DSC, and XPS, do not have a sufficient combination of spatial resolution and chemical sensitivity to determine polymer composition at nanometer length scales. To compliment our HAADF STEM imaging, we have thus employed the emerging method of spatially resolved electron energy loss spectroscopy (EELS) in the cryo-STEM.[13−16] In contrast to the sub-angstrom resolution now achievable in STEM analysis of many inorganic materials,[17] hydrated polymers are very sensitive to the ionizing radiation of the electron microscope, and the spatial resolution of our experiments is determined by the need to achieve a statistically significant ratio of signal-to-noise in spatially resolved maps of composition.[13] The electron dose to which our specimens were exposed during EELS analysis was 1200 e/nm^2, and we achieved a spatial resolution of 10 nm. Quantitative compositional analysis at 10 nm spatial resolution of polymers preserved in an aqueous medium has not been previously reported, and with this new ability to gather nanoscale compositional information, we find that the interfaces between the two lobes in these PDMS−copolymer nanoemulsion particles are substantially larger than those suggested by HAADF STEM.

Figure 2 shows low-loss EELS spectra characteristic of pure PDMS, pure MA/MMA/VAc copolymer, and pure amorphous ice. These spectra display important differences in their plasmon peak positions and in the interband transition associated with the ice band gap (∼9 eV). We used these spectra as references in a quantitative multiple-least-squares (MLS) analysis of local specimen composition[13−15] to generate maps of the water, PDMS, and copolymer distributions in individual particles. Spatially resolved data were

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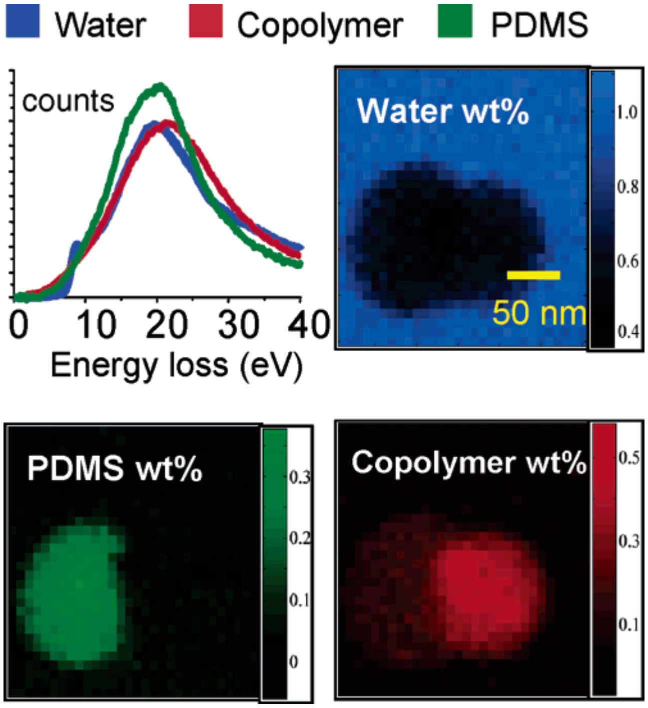

Figure 2. Low-loss EELS spectra from pure amorphous ice (blue), pure PDMS (green), and pure MA−MMA−VA copolymer (red) together with composition maps of a lobed structure nanoparticle collected at 10 nm spatial resolution by spatially resolved EELS imaging.

generated by digitally rastering an 8 nm diameter electron beam at 10 nm intervals across selected specimen areas. Figure 2 presents a typical result characterizing a single lobed nanoparticle embedded in amorphous ice.

Line profiles of composition across the particle clearly show copolymer trapped within the PDMS-rich lobe (Figure 3). In contrast, the copolymer-rich lobe contains no PDMS. This suggests that, at some point during copolymerization, pure copolymer begins to grow at the surface of the PDMS seed where it can minimize the total surface free energy by contacting the surrounding water. We speculate that the pure copolymer lobe grows both by reaction with additional monomer as well as by phase separation of growing oligomers within the increasingly incompatible PDMS phase. The fact that only trace amounts of monomer remain after polymerization indicates that the copolymer detected by EELS is derived from polymer rather than residual monomer. Because the copolymer and PDMS molecular weights are higher than their entanglement molecular weights (12 kg/mol for PDMS; 11 kg/mol for the copolymer), we conclude that some copolymer becomes kinetically trapped within the PDMS.[11]

In the PDMS−MA/MMA/VA copolymer system, an equilibrium interfacial width on the order of a few nanometers or less is expected because of the relatively high PDMS−copolymer interaction parameter. Here, however, we find that copolymer remains entrapped in the PDMS lobe over a length scale of many tens of nanometers, indicating that the heteropolymer interface is a diffuse one. This length is much larger than that suggested by the HAADF STEM contrast changes across the interface (Figure 1), indicating that the effects of interfacial curvature between the phases or of misorientation of the interface relative to the incident electron beam direction are insignificant. Importantly, with this new finding of diffuse heteropolymer interfaces, one can now conceive of new pathways to control the width of these property-defining heteropolymer interfaces based on both the equilibrium thermodynamics and the kinetic considerations which evolve dynamically during the emulsion polymerization process.

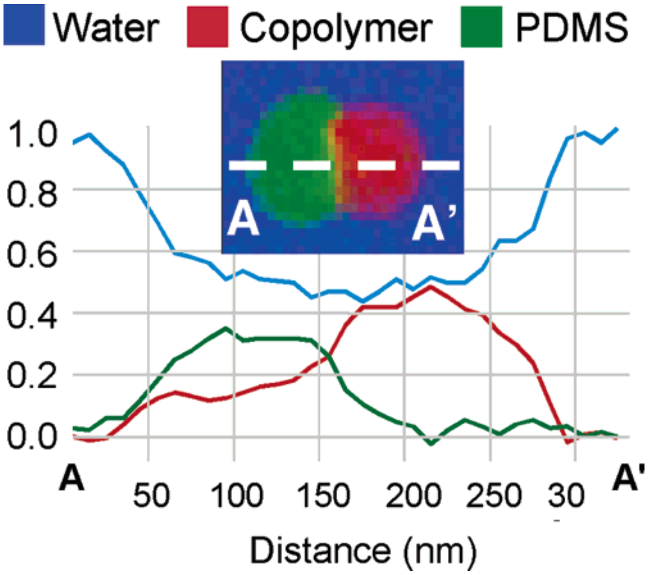

Figure 3. The weight fractions of water, MA/MMA/VAc copolymer, and PDMS across line A−A′ in the composite image of a lobed structure.

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