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Cryo-STEM EELS Mapping of Polymer Nanocolloids Preserved in Amorphous Ice

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In the development of nanosized polymeric materials having a biphasic polymer structure, the compositional distribution in the two hetero polymer phases plays an important role in determining their physicochemical properties. In particular, the compositional distribution across the interface between the two connected polymer phases in a lobed structure directly relates to the ultimate mechanical properties of these nano composite particles. Because of the fine length scales involved together, spatially resolved compositional studies of lobed polymer nanoparticles preserved in an aqueous medium has been a significant challenge. Because of its ability to collect compositional data at high spatial resolution, we use electron energy loss spectroscopy (EELS) in the cryo scanning transmission electron microscope (cryo-STEM) to quantitatively determine the nanoscale composition in two-phase particles preserved in amorphous ice.

We used low-loss EELS spectra both because of the varying valence electron structure characteristic of most polymers and solvents together with the important fact low-loss EELS can provide reasonable signals at relatively low electron dose. In contrast, the required electron dose for core-loss EELS can dramatically exceed the allowable amount dose to avoid e-beam induced radiation damage. By applying MLS fitting for low-loss spectra, Leapman et, al.[1-2] and Libera et, al.[3] could obtain quantified water maps with 60-100 nm spatial resolution in a frozen hydrated matrix. In this study, spatially resolved valence EELS with sub 10 nm spatial resolution and MLS fitting technique were used for the compositional mapping and interfacial investigation of the nano composite particles of polydimethysiloxane (PDMS) and poly[methyl acrylate (MA)-methyl methacrylate (MMA)-vinyl acetate (VA)] with/without the formation of lobed structures.[4] This enhanced spatial resolution comes from the recent installation of a much higher efficiency spectrometer and data acquisition system.

The lobed nanoemulsions were synthesized by a seeded emulsion polymerization technique where organic monomers of MMA, MA, VA were randomly copolymerized in the presence of seed PDMS emulsions. Ultrathin frozen samples were prepared by plunging thin films of emulsions supported by holey-carbon TEM grids into liquid propane. For EELS reference peaks, dried pure polymers were cryo-microtomed below the glass transition temperatures of the polymers. Imaging and spatially resolved low loss EELS spectroscopy for frozen thin specimens were done at -165 ^{o}C using a high efficiency Gatan parallel (PEELS) spectrometer combined with a 200 KeV field emission STEM. Spatially resolved data were generated by digitally rastering an 8 nm diameter electron beam with a 10 nm interpixel spacing and collecting a low-loss spectrum at each pixel position. EELS reference peaks were collected from pure aqueous phase and the cryo-microtomed sections of pure polymer components. The beam dose used for this experiment was 1200 e/nm^2.

Because there is sufficient distinction between the reference spectra characteristic of water, the copolymer and PDMS (Fig.(a)), spatially-resolved EELS and MLS fitting could be effectively performed to quantitatively map composition in various frozen nanomixtures in vitrified water under various mixing conditions, as shown in Figure (b), (c) and (d). The bright field STEM images confirm the formation of lobed nanoparticles. The combined composition map and the line profile across hetero polymer interface in a lobed particle, as shown in Figure (e), clearly indicate that the two sections of the lobed structure are physically connected by copolymer macromolecules that traverse the interface between them and formed a diffuse interface. The formation of diffuse interface which is a deviation from thermodynamically preferred case involving completed phase segregation of two immiscible polymer phases is resulted from the kinetic trapping of the copolymer within the PDMS phase. This finding also suggests new nonequilibrium pathways to control interfaces during the synthesis of multicomponent polymeric nanostructures.

References

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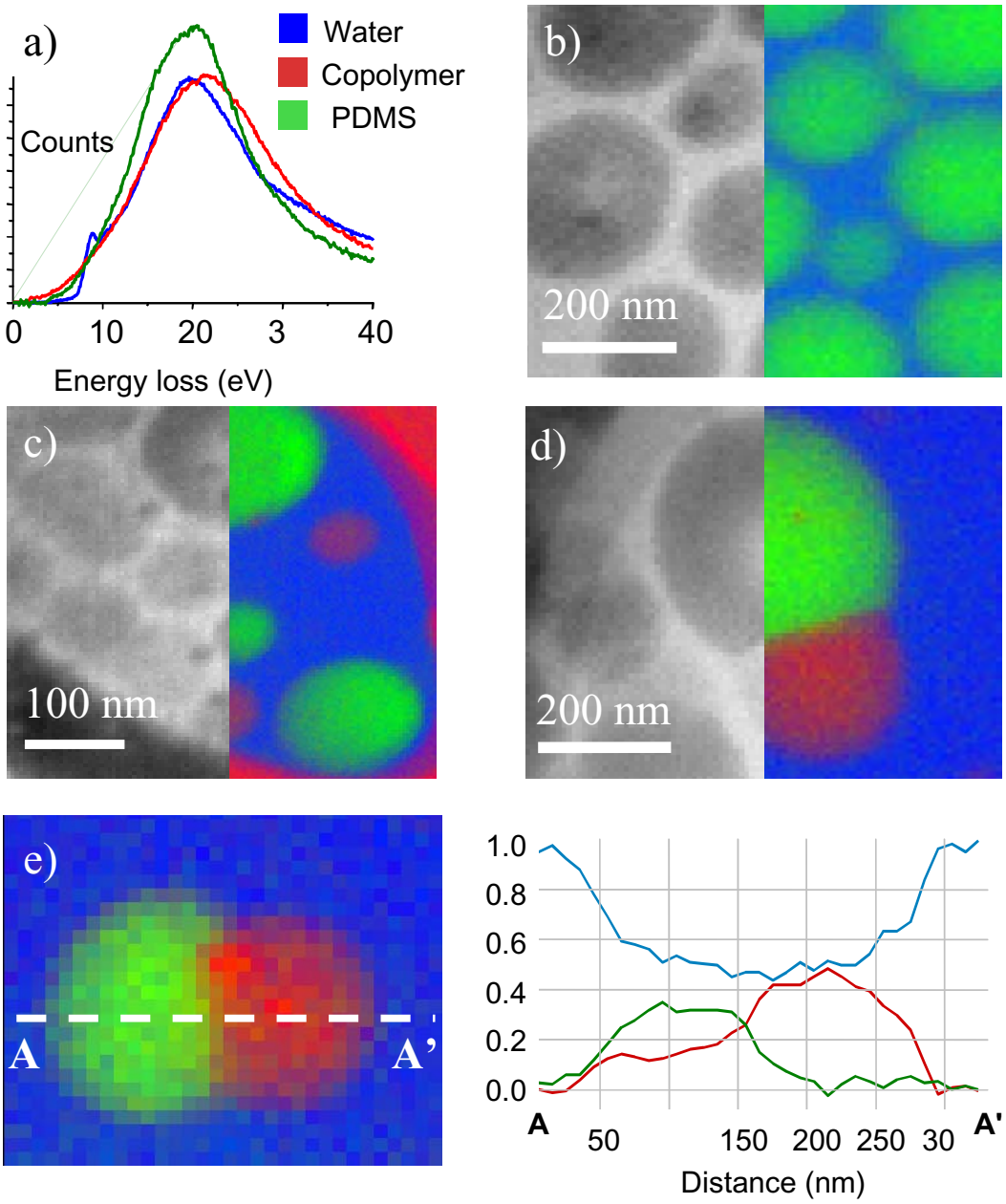

Figures; Low-loss EELS spectra from pure amorphous ice, pure PDMS, and pure MA-MMA-VA copolymer, cryo-STEM images (a), STEM images and composite maps of (b) PDMS and dissolved precursors before copolymerization; (c) simple mixture of PDMS and copolymer particles; (d) PDMS-copolymer lobed nanoparticles in vitrified ice, (e) The compositional line profiles of water (blue), MA-MMA-VA copolymer (red), and PDMS (green) across line A-A' in the composite map of a lobed structure.

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