

## Supporting Information

### **Nanofibrillar micelles and entrapped vesicles from biodegradable block copolymer/polyelectrolyte complexes in aqueous media**

Nisa V. Salim, Nishar Hameed, Tracey L. Hanley, Lynne J. Waddington, Patrick G. Hartley,  
and Qipeng Guo

**Sample Preparation.** The block copolymer PEO-*b*-PLA was first dissolved in THF to prepare a 1 % (w/v) of polymer solution. Complexes were prepared by slowly adding PAA solution in water into PEO-*b*-PLA solution to make a mixture of PEO-*b*-PLA/ PAA with a desired molar ratio. Subsequently the solutions were mixed together, stirred for 5 hr, and stored at room temperature. Then a given volume of deionized water was added into the polymer mixture to make it 3 wt% and stirred for 1 day to allow polymer chains for exchange. Finally, the system was then quenched into an excess of water before they were dialyzed to remove THF. The appearance of cloudiness in the solution indicated that aggregation had taken place. We investigated the changes in the morphology in two ways, first by varying the molar ratios of [AA]/[EO] from 0.2 to 1 and then the water content was varied between 9 wt% to 20 wt% at each molar ration to see the change in aggregate morphologies. The obtained complexes were used for further experiments.

**Cryo-TEM Sample Preparation.** A laboratory-built humidity-controlled vitrification system was used to prepare the samples for imaging in a thin layer of vitrified ice using cryo-TEM. Humidity was kept close to 80% for all experiments, and ambient temperature was 22°C. 200-mesh copper grids coated with perforated carbon film (Lacey carbon film: ProSciTech, Qld, Australia) were used for all experiments. 4µl aliquots of the sample were pipetted onto each grid prior to plunging. After 30 seconds of adsorption time the grid was blotted manually using Whatman 541 filter paper, for approximately 2 seconds. Blotting time was optimised for each sample. The grid was then plunged into liquid ethane cooled by liquid nitrogen. Frozen grids were stored in liquid nitrogen until required.