Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information for Liquid-liquid phase separation induced auto-confinement

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Materials and Instruments:

All TEM experiments were performed on a JEOL 2100 equipped with a 200 keV field emission gun and a OneView camera, Irvine Materials Research Institute, University of California, Irvine. Optical imaging was performed using a Keyence Bz-X810 all in one microscope, all samples were imaged between two glass coverslips. All solvent switch experiments were carried out using a Infusion ONE New Era single channel syringe pump along with a 4.7mm thick 1mL syringe.

Terminology

The growing body of literature of phase separation and block copolymer self-assembly has a lot of terminology to follow. For ease of understanding, here we provide some clarification on the terms used in the main text.

In this work we use the term *coacervate* to describe polymer rich droplets that form via liquid-liquid phase separation (LLPS).[1,2] While these droplets may resemble emulsions,[3] our system is not an emulsions as all solvents used are miscible amongst one another. Typical block copolymer emulsions are prepared with a mixture of solvents like, toluene and water.

Confinement of polymers can be achieved in many ways; in our work we compare our observation of auto-confinement to those of confinement emulsion systems. We coin the term *auto-confinement* here as the confinement experienced by the polymers occurs from droplets made of those polymers themselves, instead of an oil/water emulsion.

Membrane thickness of PS_{200}-*b*-PAA_{35} vesicles

A polystyrene chain fully extended of 200 units will be around 30nm, based on L = Nb, where, L is the contour length, N is the monomer units (200), and b is the bond length between monomers (0.154 for C-C). Based on this, a fully extended PS_{200} block will have an L of 30nm and form a bilayer of about 60nm when fully stretched. The membrane thickness of the vesicles formed in Pathway 1 is 43± 4nm. The thinner membrane measurement compared to the fully stretched calculation is expected here as the relationship between polymer contour length and membrane thickness is highly variable depending on the vesicle preparation process.[4]

Self-assembly and characterization of PS_{200}-*b*-PAA_{30}:

Cryo-electron microscopy of block copolymer assemblies

Quantifoil Holey Carbon Films were purchased from Electron Microscopy Sciences, grids were glow discharged for 70 s to increase hydrophilicity prior to sample preparation. Vitrification was carried out by an Automatic Plunge Freezer ME GP2 (Leica Microsystems) where sample preparation onto cryoTEM grids was carried out at 95% humidity to prevent evaporation and blotted for 3 s before auto-plunging into liquid propane. Vitrified samples were studied on a JEOL-2100F TEM using a Schottky type field emission gun operating at 200 kV. Size measurements for cryoTEM images were performed using the measurement tool in ImageJ.

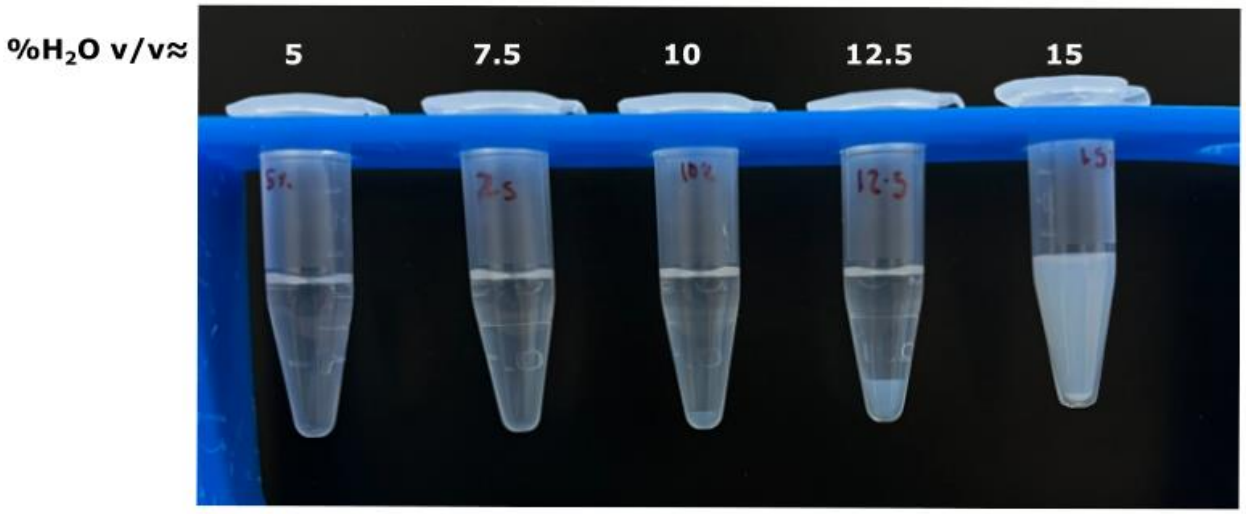

Figure S1: Photograph of PS_{200}-*b*-PAA_{30} in 1:4 THF:Dioxane with increasing water content v/v% to map out the phase trajectory.

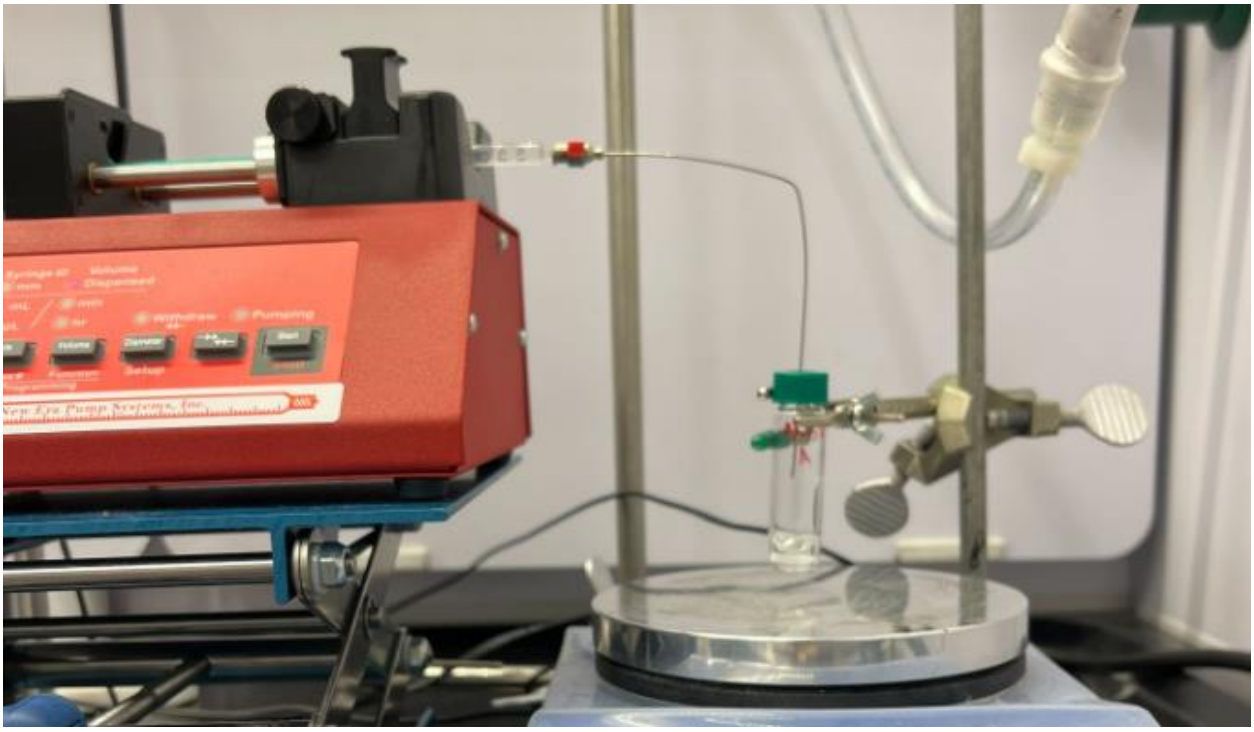

Figure S2: Photograph of a typical self-assembly apparatus using a syringe pump to add in the selective solvent. All self-assembled particles in this study were prepared using this exact set up. A stock solution of dissolved polymer was added to a vial with a stir bar and sealed using a septum cap. Water was syringed at the rate of 0.2 mL/min while the solution mixture was stirred vigorously. For each experiment, the same syringe was used to have the same droplet volume at the rate of 0.2 mL/min. For 1 mL assembly, the solvent duration to reach 50% water was 1 hour. For cryo-EM imaging, 100 µL of the self-assembly solution at 50% water was dialyzed in mini dialysis tubes (MWCO 3.5 kDa) over night.

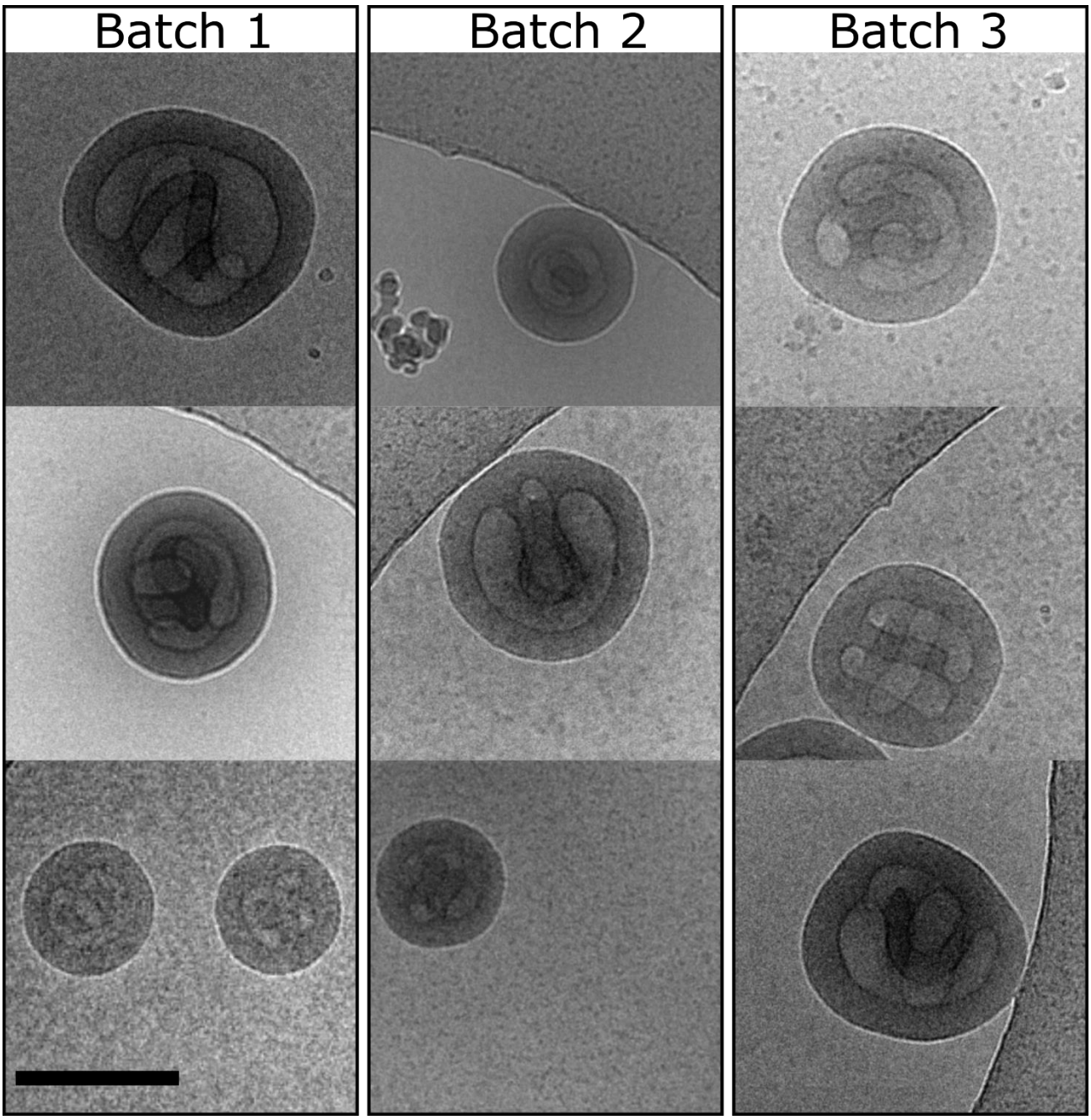

Figure S3: Cryo-EM images of confined morphologies prepared via Pathway 2 from different batches, all at 10 mg mL^{-1} initial polymer concentrations. Scale bar = 200 nm.