ELECTRONIC SUPPLEMENTARY INFORMATION

Probing the Morphology Evolution of Chemically Anisotropic Colloids Prepared by Homopolymerization- versus Copolymerization-Induced Phase Separation

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Synthesis of Non-Crosslinked Polystyrene (PS) Seed Particles

Non-crosslinked polystyrene (PS) seed particles were synthesized by dispersion polymerization. In a 100 mL round bottom flask, 0.03 g poly(vinylpyrrolidone) (Sigma-Aldrich, 40,000 g/mole) was dissolved in 75 mL isopropyl alcohol (Fisher Scientific, Certified ACS). A solution of 0.02 g ammonium persulfate (Sigma-Aldrich, 98%), 9 mL DI water (18.2 mΩ/cm), and 6.6 mL styrene (Sty, Sigma-Aldrich, 99%) was then added to the round bottom flask. The solution was purged with nitrogen for 5 minutes and then tumbled at 40 rpm in a 70°C oil bath for 24 hours. After polymerization, the particles were washed thoroughly with DI water by alternating centrifugation (4500 rpm, 25 mins, 20±1°C) and sonication (23±3°C).

Synthesis of Anisotropic Colloids by Seeded Emulsion Polymerization (SEP)

A 1.0 mL dispersion was prepared containing 20 vol% PS seed particles in an aqueous solution with 1 wt.% poly(vinyl alcohol) (PVA, Aldrich, 13,000-23,000 g/mole, 87-89% hydrolyzed). The dispersion was diluted to 4.0 mL with DI water. A monomer emulsion was prepared separately by combining a monomer mixture (200-800 µL) of Sty and/or *tert*-butyl acrylate (*t*BA, Aldrich, 98%) with 0.5 wt.% initiator 2,2′-azobis(2,4-dimethylvaleronitrile) (Wako V-65) in a 3.2 mL aqueous solution containing 1 wt.% PVA; the mixture was vortexed for 60 seconds to form an emulsion. Seed particles were mixed with the monomer(s) and initiator solution by adding the seed particle dispersion to the monomer emulsion in an 8 mL vial; the vial was rotated (60 rpm) for 24 hours to facilitate mixing. Polymerization was performed by tumbling (100 rpm) the seeded emulsion in a 70°C oil bath for 24 hours. After polymerization, the particles were washed thoroughly with DI water by alternating centrifugation (4500 rpm, 25 mins, 20±1°C) and sonication (23±3°C).

Acid-Catalyzed Hydrolysis (ACH) and Selective Dissolution

Post-synthetic modification of the anisotropic colloids was done by ACH of *t*BA-containing polymer using trifluoroacetic acid (TFA, Sigma-Aldrich, 99%) forming water-soluble acrylic acid (AA)-containing polymer. To a glass vial containing 60 mg of washed particles (produced by either homo-PIPS or co-PIPS in SEP), 2 mL of TFA was added along with a magnetic stir bar. The vial contents were stirred (350 rpm) for 24 hours; the particles were then washed by alternating centrifugation (4500 rpm, 25 mins, 20±1°C) and sonication (23±3°C). The first wash was performed with ethanol to adjust the continuous phase density, and subsequent washes were performed using DI water with a single wash at elevated pH in a 0.1 M sodium hydroxide (NaOH) aqueous solution to facilitate dissolution of the AA-containing polymer. All subsequent washes were performed with DI water to remove residual NaOH.

Characterization of Emulsion Droplet and Anisotropic Colloid Size by Dynamic Light Scattering (DLS)

Colloid and emulsion droplet size distributions were measured by DLS (Malvern Panalytical Zetasizer Nano ZS). The size distributions based on scattering intensity are given in **Figure S1**, and the corresponding Z-average diameter and polydispersity index (PDI) are provided in **Table S1**. All samples were prepared with a monomer feed-to-seed volume ratio of 80/20. Samples prepared by homo-PIPS contained 100 vol% *t*BA in the monomer feed, while samples prepared by co-PIPS contained 50/50 vol% *t*BA/Sty in the monomer feed.

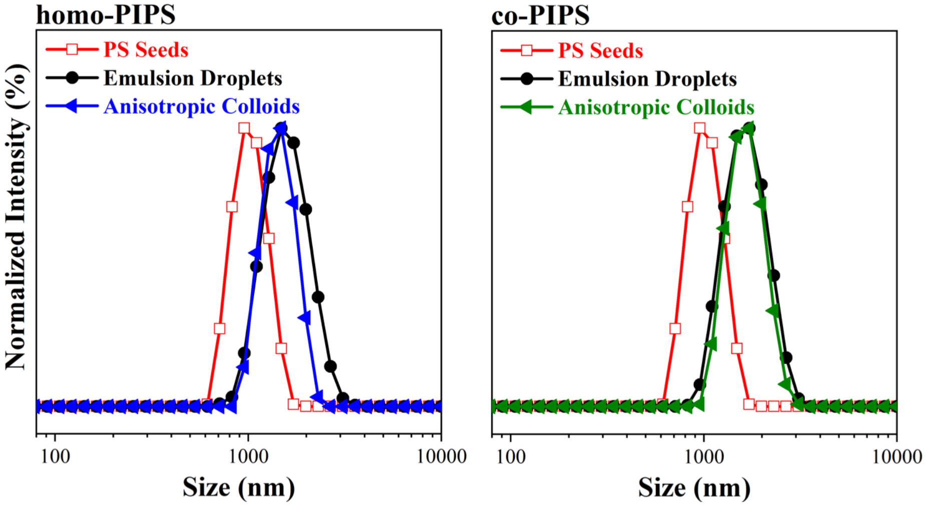

Figure S1. DLS size distributions for the non-crosslinked PS seed particles, seeded emulsion droplets, and anisotropic colloids produced by homo-PIPS and co-PIPS during SEP.

Table S1. Particle and emulsion droplet Z-average diameter and PDI measured by DLS.

Preparation Method	Sample	Z-average Diameter (nm)	PDI
Dispersion Polymerization	PS Seed Particles	1005	0.057
Homo-PIPS in SEP	Emulsion Droplets	1534	0.087
	Anisotropic Colloids	1406	0.053
Co-PIPS in SEP	Emulsion Droplets	1575	0.075
	Anisotropic Colloids	1610	0.044

Characterization of Colloids by Electron Microscopy

Images included in the main text of the manuscript were imaged by scanning electron microscopy (SEM) using a FEI Magellan 400 XHR scanning electron microscope operating at 5.00 kV and transmission electron microscopy (TEM) using a JEOL JEM-2000FX transmission electron microscope (TEM) operating at 200 kV.

Before SEM, colloids were sputter-coated with a thin layer of platinum (Pt, 3-5 nm, Cressington 208HR). The SEM electron beam causes significant degradation by crosslinking, bond scission, and mass loss in situ giving the appearance of a wrinkled surface to the P*t*BA homopolymer and poly(Sty-*co*-*t*BA) copolymer (with monomer feed ≥50 vol% *t*BA) before ACH (**Figure S2a**). The electron beam damage is less severe in the copolymerized particles than the homopolymerized particles due to decreasing acrylate content. Polystyrene is more stable to beam damage than acrylate containing polymers due to the aromaticity of the pendant phenyl groups and is not as visibly affected (Sawyer, 2008). The surface wrinkling is likely caused by the buckling of the Pt thin film as the P*t*BA-containing polymer beneath the film degrades. The most significant beam damage is seen in colloids with the highest acrylate content produced by homo-PIPS using 100 vol% *t*BA in the monomer feed. Before significant beam damage, the particles are near spherical with discernible surface texture. This can be seen by imaging the Pt-coated particles at low magnification and enlarging the micrograph (**Figure S2b**). Beam damage of the non-coated particles (100 vol% *t*BA) is also evident upon stepwise irradiation with increasing acceleration voltage (**Figure S2c**).

Reference: L.C. Sawyer, D. T. Grubbs, and G. F. Meyers, Polymer Microscopy, Springer, New York, 2008.

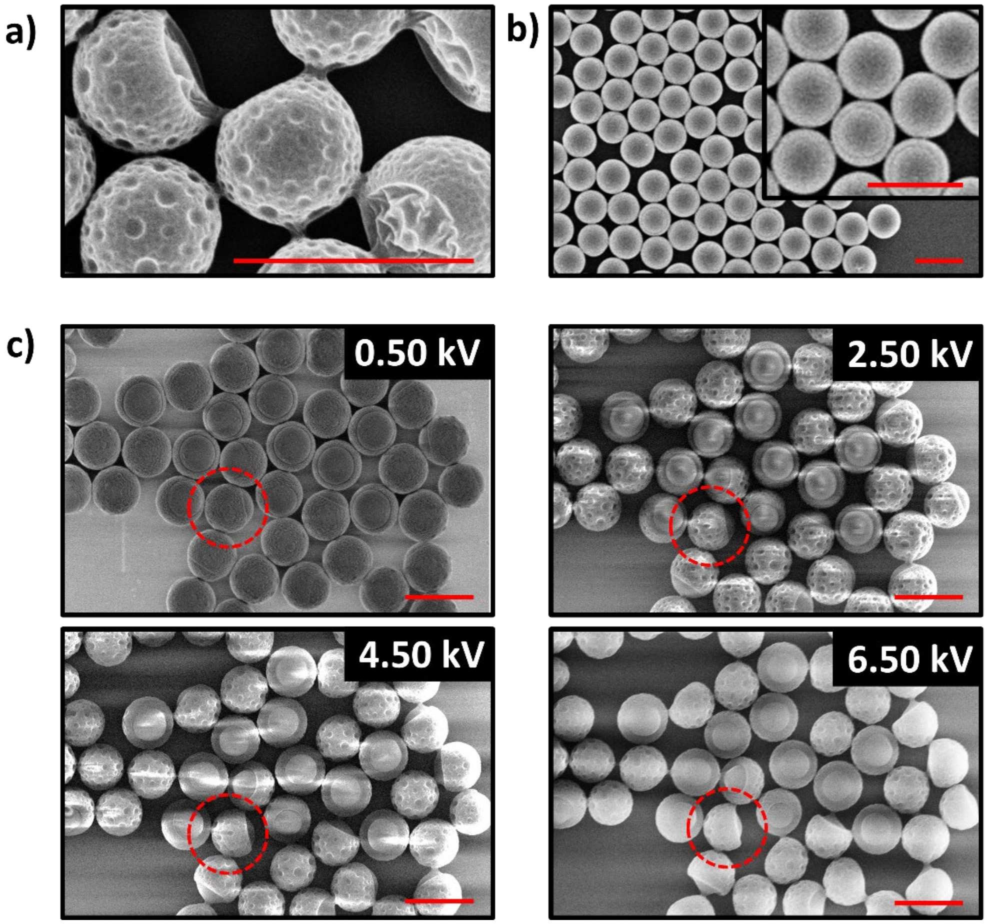

Figure S2. SEM images of particles prepared by homo-PIPS with 100 vol% *t*BA in the monomer feed. Images were collected using our standard conditions (5.0 kV) with Pt coating at (a) high magnification (25,000x) and (b) low magnification (5,000x); the low magnification micrograph is enlarged in the inset. (c) The same particles imaged (12,500x) without a Pt coating are shown with increasing acceleration voltage, 0.50, 2.50, 4.50, and 6.50 kV. The same particle is circled in each micrograph for reference. Scale bars represent 2 μm.

Fourier Transform Infrared (FTIR) Spectroscopy

Particle composition was analyzed by FTIR in attenuated total reflectance (ATR) mode (Spectrum One FTIR spectrometer, Universal ATR sampling accessory, PerkinElmer) with a diamond/ZnSe crystal in the range of 4000-650 cm^{-1} (step size of 4.0 cm^{-1}). Analysis confirmed the composition of the non-crosslinked PS seeds and the anisotropic colloids produced by SEP with varying monomer feed composition before and after post-synthetic modification by ACH (Figure 2a,b,d,e,g,h,j,k). The presence of the strong signal at 1725 cm^{-1} associated with the carbonyl

(-C=O) stretching vibration of *t*BA in the as-synthesized colloids confirms incorporation of *t*BA during SEP. The absence of the *t*BA carbonyl peak and the presence of weak signal associated with the AA carbonyl at 1705 cm^{-1} after ACH indicate that the *t*BA-containing polymer is converted to AA-containing polymer and that most of this polymer is subsequently dissolved with washing. Residual AA moieties in the particles are likely a consequence of two factors: (i) incomplete phase separation by polymerization-induced phase separation (PIPS) during SEP and (ii) decreasing *t*BA content in the copolymer. PIPS using a neat monomer feed leads to kinetically-trapped morphologies (see Figure S4 below) for which chain dynamics would play a role in the dissolution of water-soluble polymer from the colloid interior. Additionally, as the *t*BA content in the copolymer decreases, a solubility limit is likely reached at which point there is not sufficient AA content for dissolution.

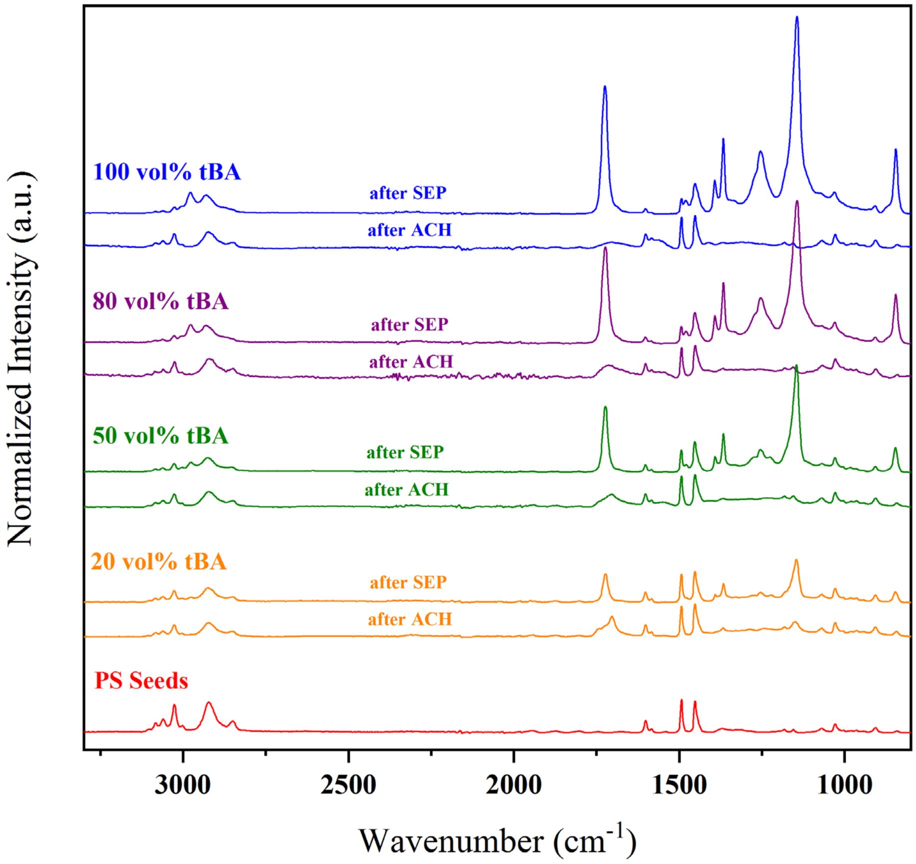

Figure S3. FTIR spectra of non-crosslinked PS seed particles and anisotropic colloids as-synthesized and after ACH with decreasing *t*BA content in the monomer feed as follows: 100, 80, 50, and 20 vol%. All spectra were normalized to 1452 cm^{-1}.

Solvent-Assisted Phase Separation (SAPS)

To confirm whether the morphology of the anisotropic colloids is kinetically-trapped, we performed SAPS. Aqueous dispersions (24 mL) containing 1 wt.% PVA and 0.1 vol% colloids were mixed with toluene at a colloid/toluene volume ratio of 10/90. The mixture was heated to 70±5°C in an oil bath and stirred (150 rpm). After a 24-hour equilibration period, toluene was evaporated by removing the vial cap and maintaining 70±5°C in the oil bath while stirring (150 rpm). SAPS transformed as-synthesized patchy-Janus colloids into phase separated Janus particles with smooth faces.

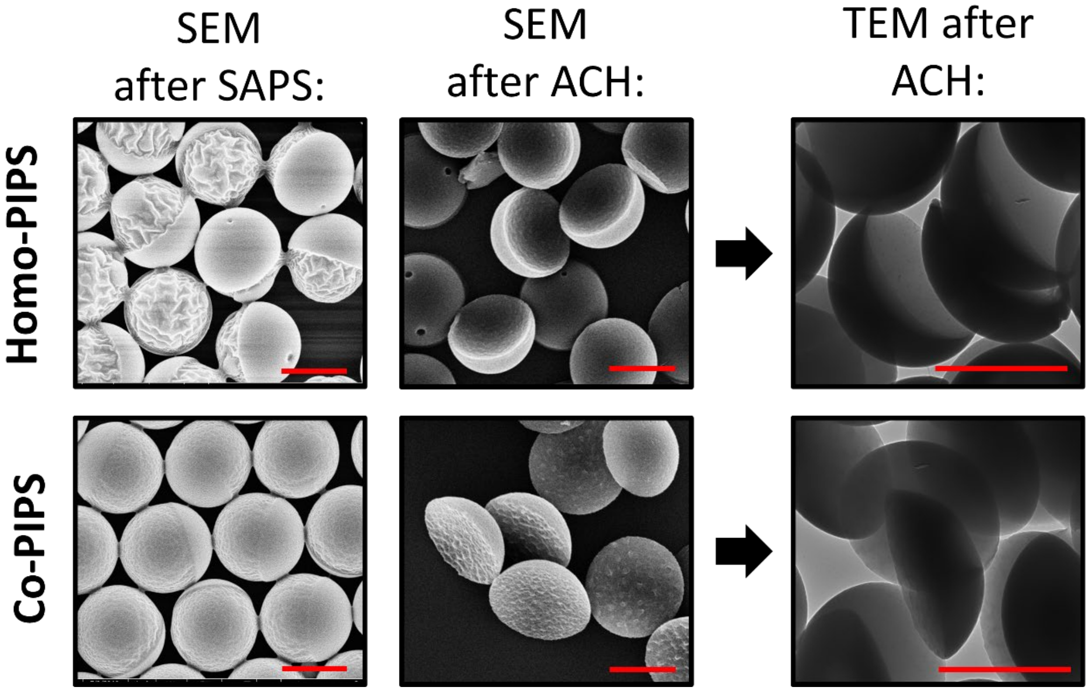

Figure S4. SEM images of the colloid morphology after SAPS and subsequent ACH. Homo-PIPS was performed with a monomer feed consisting of 100 vol% *t*BA, and co-PIPS was performed with a monomer feed consisting of 50/50 vol% *t*BA/Sty. The monomer feed-to-seed volume ratio was 20/80. Scale bars represent 1 μm.

Characterization of Colloid Morphology Evolution by TEM

The morphology evolution of colloids produced by homo-PIPS and co-PIPS was characterized by TEM to visualize the internal morphologies and microdomain structures after ACH.

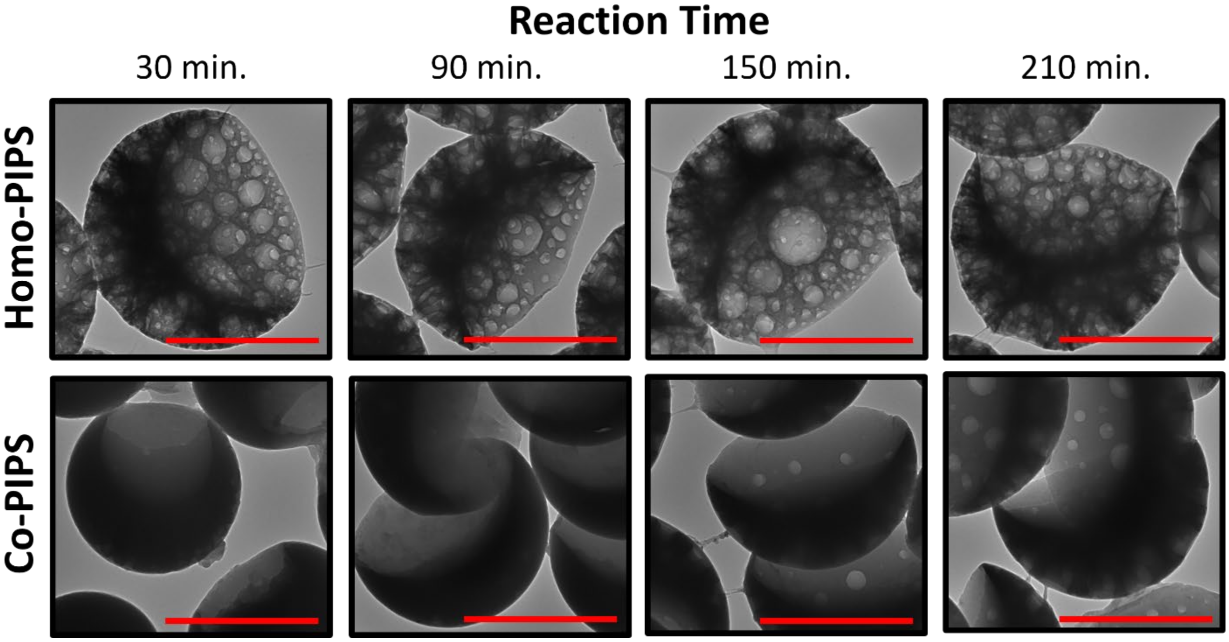

Figure S5. TEM images of the colloid morphology evolution produced by homo-PIPS (100 vol% *t*BA in the monomer feed) and co-PIPS (50/50 vol% *t*BA/Sty in the monomer feed). All particles are imaged after post-synthetic modification by ACH to visualize the internal morphologies. Scale bars represent 1 μm.