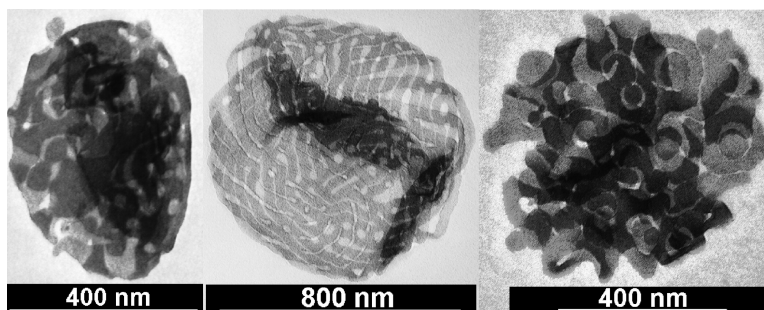


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Hierarchical Interfacial Assembly of ABC Triblock Copolymer

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In a block-selective solvent, a block copolymer (BC) may self-assemble into micelle-like aggregates (MAs) with shapes ranging from spheres to cylinders, vesicles, tubes, and donuts, etc.^{1–9} Further assembly of these MAs or the hierarchical two-tier assembly of BCs may lead to functional “superstructures”. For example, assembly of MAs into 2-D superlattices on substrate surfaces has allowed the lattices to be used as lithographic¹⁰ or electrochemical masks¹¹ for production of inorganic nanoparticle arrays with potential applications as memory or electronic devices. Hierarchical assembly, allowing molecular order and structural control at multilength scales, is the basis of life itself.^{12–13} Despite its importance, it has been seldom practiced for BCs in solvents, and literature examples on this subject have so far included further self-assembly of metastable BC MAs toward more stable superstructures^{14–15} and the further self-assembly of MAs by changing the solution pH or ionic strength, etc.¹⁶ While superstructures from these hierarchical self-assembly processes can be diverse, they are not well understood to warrant the prediction of the shape and size of superstructures that can be prepared. In this communication we report a method for the hierarchical interfacial assembly of a BC invariably into spherical “superaggregates” (SSAs) with different surface morphologies. These SSAs, which are hundreds of nanometers in size or larger, are formed via MA adsorption and fusion on surfaces of droplets of one liquid dispersed in another.

Particles adsorb at the interface of two immiscible liquids because of the Pickering effect or a decrease in the system's free energy by satisfying $\gamma_{12} > |\gamma_{1P} - \gamma_{2P}|$,^{17–18} where γ_{12} , γ_{1P} , and γ_{2P} denote the interfacial tensions between liquids 1 and 2, between liquid 1 and the particles, and between liquid 2 and the particles, respectively. This effect has so far been used to stabilize emulsions and to prepare microcapsules with walls consisting of latex spheres,¹⁷ magnetic spheres,¹⁹ clay particles, quantum dots,²⁰ bioparticles,²¹ homopolymer microrods,²² and carbon nanotubes.²³ More recently it has been used by the Armes group to prepare stimuli-responsive emulsions using crosslinked BC micelles as the stabilizer.²⁴ To our knowledge, there have been no reports on the assembly of “dynamic structures” like spherical MAs (SMs) or cylindrical MAs (CMs) of BCs using the Pickering effect.

The CMs and SMs of a polyisoprene-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) or PI-PCEMA-PtBA sample were assembled in this study (Triblock structure shown in the Supporting Information or SI). This triblock consisted of 110 isoprene, 150 CEMA, and 320 tBA units. The CMs were prepared in decahydronaphthalene (DN) by heating the polymer at 60 °C for 3 d. The SMs were prepared by adding DN into a solution of the BC in CH₂Cl₂ and then removing CH₂Cl₂ by N₂ bubbling. The MAs possessed an insoluble PCEMA core and a soluble PI and PtBA mixed corona. Figures 1a and 2a show transmission electron microscopy (TEM) images of the CMs and SMs with PI and PCEMA stained by RuO₄. The cylinders could be straight, branched, or looped. The SMs coexisted with some short cylinders. The TEM diameters of the CMs and SMs were 20.4 ± 0.8 and 21.9 ± 1.7 nm, respectively.

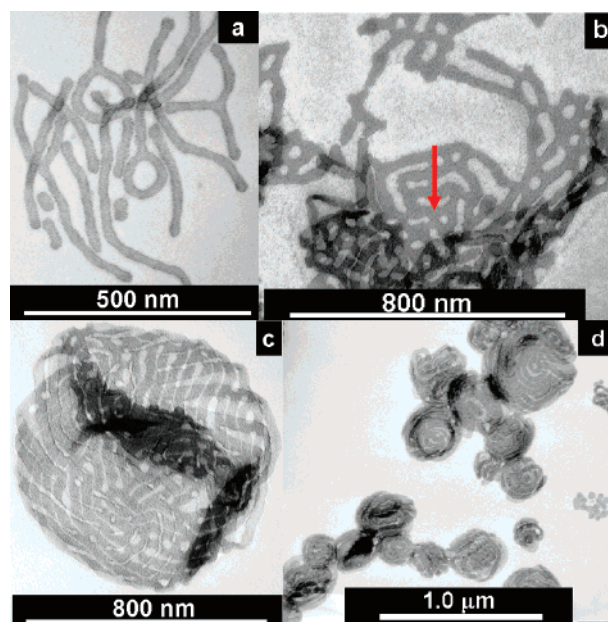


Figure 1. TEM images of CMs (a) and CM superaggregates formed at 52 ± 2 °C 5 min (b) and 3 d (c and d) after MeOH addition.

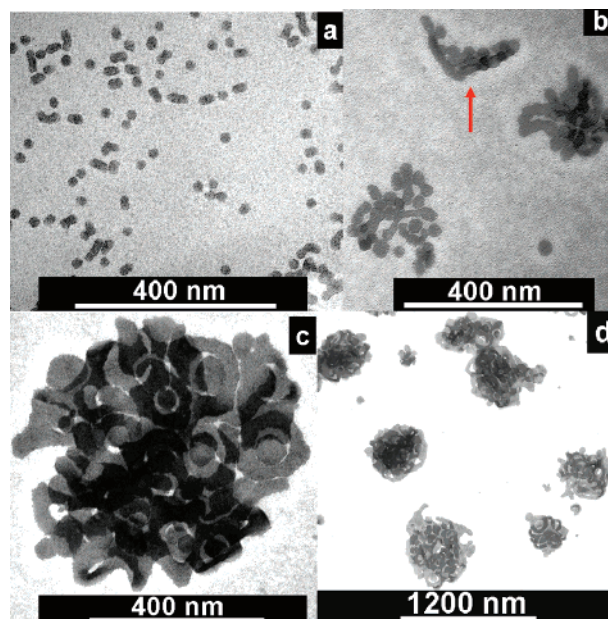


Figure 2. TEM images of SMs (a) and SM superaggregates formed at 22 ± 2 °C 5 min (b) and 2 d (c and d) after MeOH addition.

MAs were assembled by adding methanol (MeOH) at $V_{DN}/V_{MeOH} = 3/1$ to the CM or SM solutions in DN and stirring the resultant mixture at 22 ± 2 or 52 ± 2 °C for 1–7 d. MeOH was used as liquid 2 because it was immiscible with DN and solvated only PtBA. The fact that a cloudy bottom Pickering layer separated from a top

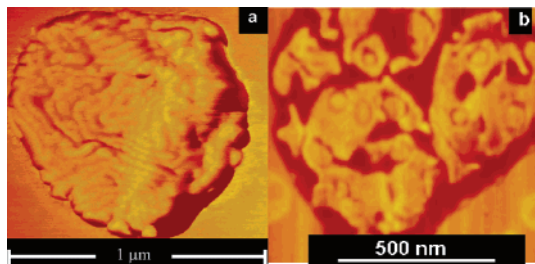


Figure 3. AFM tapping-mode phase images for a ribbon cage (a) from CMs and several flowery SSAs (b) from SMs.

MeOH-rich layer 1–3 h after stirring stopped and the layer remained stable for weeks or longer in all four cases involving two types of MAs at two temperatures T suggested MA assembly. This assembly was proven unambiguously by the observation of fluorescence from only the rim of the droplets when a fluoresceinamine-tagged PI-PCEMA-PtBA sample was used to prepare the SSAs (Figure 8, SI).

Our cryo-TEM images had poor contrast. The CM and SM assembly after MeOH addition was better followed by routine TEM. Specimen preparation in this case involved the aspiration of the DN/MeOH solutions onto carbon-coated copper grids, sample drying, and then sample staining by RuO₄. Figures 1b and 2b show TEM images for the superaggregates formed 5 min after MeOH addition into the CM and SM solutions at 52 ± 2 and 22 ± 2 °C, respectively. The original individual CMs and SMs have assembled in some cases into bowl-shaped superaggregates (marked by red arrows in Figures 1b and 2b). While the 2-D projections of many particles in Figure 2b are still circular, the average diameter of the circles increased from 21.9 ± 1.7 nm in Figure 2a to 36.0 ± 6.1 nm in Figure 2b, suggesting the flattening or fusion of the SMs. The fusion of the CMs is evident in Figure 1b, where no individual cylinders but cylinder ladders and networks are seen. The CMs probably also flattened because the TEM width in Figure 1b is 33.9 ± 5.6 nm rather than 20.4 ± 0.8 nm as in Figure 1a. Undisputable evidence for particle flattening at the DN/MeOH interface was obtained from a study of superaggregates of cross-linked PI-PCEMA-PtBA CMs. At a CEMA double bond conversion of 15%, the crosslinked CMs did not fuse but assembled at the DN/MeOH interface (SI). The assembled cross-linked CMs had a width of 27.0 ± 2.6 rather than 20.4 ± 0.8 nm.

Figure 1c and d show TEM images of the SSAs formed at 52 ± 2 °C from CMs 3 d after MeOH addition and Figure 2c and d show TEM images of SSAs of SMs 2 d after MeOH addition at 22 ± 2 °C. These structures were unchanged up to the longest observation time of 7 d. At 52 ± 2 °C the SSAs were ribbon cages. The SSAs were flower-like at 22 ± 2 °C in which some SMs had fused into ribbons surrounding deformed “balls” resulting in a “ball in socket” surface morphology. While the observed structures were the “dried” versions of the SSAs in DN/MeOH, their diversity and their reasonable evolution with time suggest the close correlation between the “wet” and “dry” structures. We further speculate that the ribbon cages and flowery SSAs were the equilibrium structures because they were formed at 52 ± 2 and 22 ± 2 °C, respectively, regardless of whether the CMs or SMs were used as the assembling block initially at a given T (SI).

Atomic force microscopy (AFM) specimens were prepared by aspirating samples on silicon and the topographic analyses showed that the SSAs had height to diameter ratios less than 1/2 suggesting deflated SSAs due to solvent evaporation. Figure 3 shows AFM phase images for a ribbon cage and several flowery SSAs. Fragmentation appears to have occurred for some flowery SSAs,

but the surface morphologies of the intact parts of the SSAs appear similar to those deduced from TEM.

The total free energy F_{tot} of the adsorbed and fused MAs has contributions from the interfacial tensions, the stretching of the PtBA and PI chains, and the compression of the PCEMA core chains. Minimization of the system’s interfacial tension requires PCEMA to form a continuous layer, which is counteracted by increases in the stretching energies for the PI and in particular the longer PtBA chains and the compression energy for PCEMA. The equilibrium surface morphologies of the fused MAs thus correspond to those that help minimize F_{tot} . A major difference between the ribbon cages and the flowery SSAs is the PCEMA ribbon spacing, which appears to be larger in the cages. A larger spacing, which is probably filled by the PtBA chains, is favored at the higher T probably for the higher PtBA chain expansion and a lower γ_{12} . A lower γ_{12} helps reduce PCEMA ribbon flattening and fusion, and a lower γ_{12} at 52 ± 2 °C can be appreciated from the observed larger miscibility between DN and MeOH at this T (SI).

In summary, we have demonstrated the hierarchical assembly of PI-PCEMA-PtBA CMs and SMs at the interface of DN/methanol via the Pickering effect and the fusion of the adsorbed MAs into SSAs with different surface morphologies at different T . The generality of this phenomenon remains to be discovered.

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Supporting Information Available: Discussion of polymer characterization, micelle preparation and assembly, and more microscopy images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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