

Supporting Information for

**Electrostatic Self-Assembly of Polystyrene Microspheres
Using Chemically-Directed Contact Electrification**

Logan S. McCarty, Adam Winkleman, and George M. Whitesides*

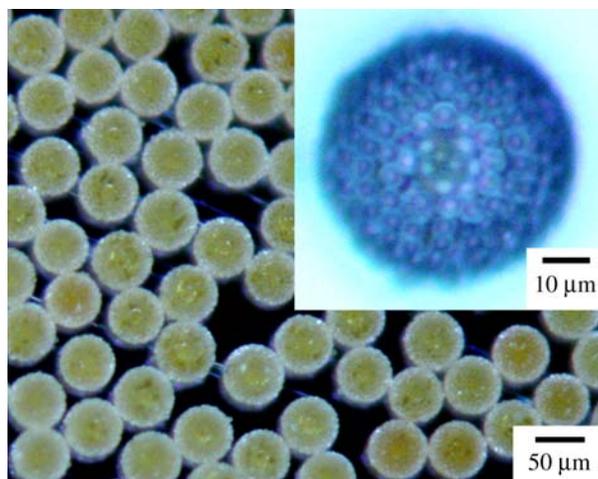


Figure S1. Optical micrographs of the assemblies resulting from a combination of 50- μm -diameter negatively-charged orange spheres and 5- μm -diameter positively-charged colorless spheres. The large dark-field image shows the high yield and uniformity of the assemblies; the inset shows a bright-field image of a single representative assembly.

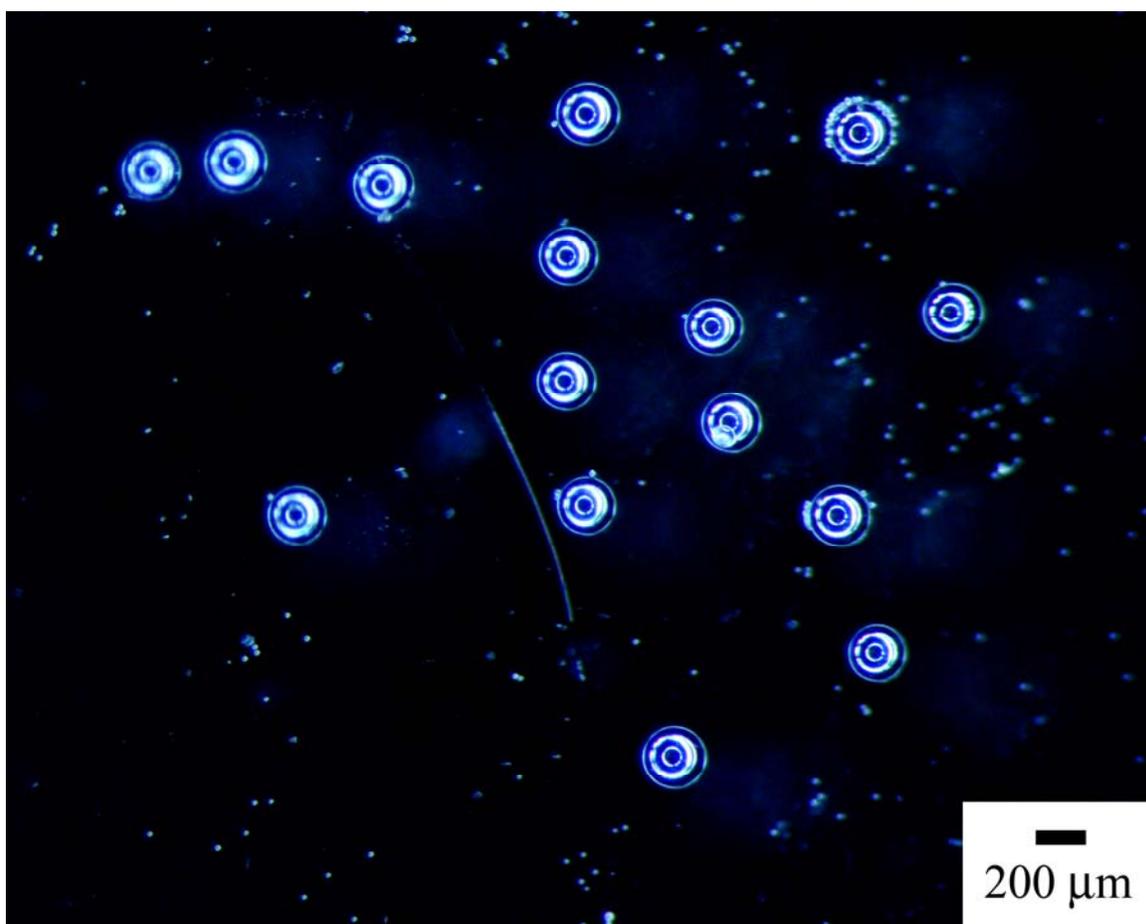


Figure S2. An optical micrograph of the results of a control experiment involving a combination of unfunctionalized 200- μm polystyrene spheres and unfunctionalized 20- μm polystyrene spheres.

Experimental Details

Unless otherwise specified, all chemicals and solvents were purchased from Aldrich and used as received. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ).

Chloromethylation of Polystyrene Beads. Following a literature procedure,^[1] we combined 500 mg of crosslinked polystyrene beads (poly(styrene-*co*-divinylbenzene), 70 μm diameter, Duke Scientific) and 450 mg of *s*-trioxane in a 20-mL flask. Under nitrogen, 5.0 mL of anhydrous chloroform, 1.9 mL of Me_3SiCl , and 0.3 mL of SnCl_4 were added and the mixture was stirred at room temperature. After 30 minutes, the beads had developed a dark brick-red color. After a total of two hours, the reaction was quenched by adding a mixture of 20 mL of THF and 10 mL of methanol; the color vanished almost immediately. The beads were collected by filtration, washed three times with 30-mL portions of THF, washed twice with 10-mL portions of hexanes, and dried under vacuum at room temperature overnight. A total of 546 mg of slightly off-white beads were collected. Anal. found: C, 86.79; H, 7.58; Cl, 5.87. Based on this analysis, 19% of the styrene residues in the polymer had been chloromethylated, for a degree of functionalization (DF) of 0.19. Polystyrene beads with other diameters (also from Duke Scientific) were functionalized using the same procedure, with the following results: 200 μm , 8.87% Cl by mass (DF = 0.30); 100 μm , 5.92% Cl (DF = 0.19); 50 μm , 6.96% Cl (DF = 0.23); 25 μm , 7.04% Cl (DF = 0.23); 20 μm , 5.46% Cl (DF = 0.17); 5 μm , 7.56% Cl (DF = 0.25).

Preparation of Tetraalkylammonium Beads, 1. To 10 mL of N-methylpyrrolidinone (NMP) was added 100 mg of chloromethylated polystyrene beads and 56 mg of quinuclidine. The mixture was stirred at room temperature overnight. The beads were collected by filtration, washed twice with 20-mL portions of ethanol, twice with 20-mL

portions of DMF, three times with 20-mL portions of THF, and three times with 20-mL portions of ethanol. (Ethanol does not swell the polystyrene resin, while DMF and THF do; this sequence of washes was used in order to rinse the beads, swell them, remove polar contaminants with DMF and nonpolar contaminants with THF, and then deswell the beads back to their original size.) The resulting colorless beads were dried in an oven at 60 °C and stored in a glass vial under ambient conditions. Anal. found (200- μ m beads): C, 80.26; H, 7.59; N, 1.15; Cl, 7.67. The observed N content suggests that the reaction with quinuclidine was only ca. 40% complete. We note that the crosslinked polystyrene purchased from Duke Scientific is ~10% crosslinked, whereas typical solid-phase synthesis resins are ~1% crosslinked. The highly-crosslinked beads swell in NMP to only ~1.5 times their volume, while the usual beads swell to about 10 times their volume. Our bulk yields tended to be low as a result.

Preparation of Azo-Sulfonate Beads, 2. To 10 mL of DMF was added 100 mg of chloromethylated polystyrene beads and 40 mg (120 mmol) of sodium 4-hydroxyazobenzene-4'-sulfonate (prepared by a literature procedure).^[2] The resulting yellow solution turned orange upon the addition of 0.04 mL (110 mmol) of 2.7 M sodium ethoxide in ethanol. The mixture was stirred at 100 °C overnight. The beads were collected by filtration, washed twice with 20-mL portions of water, twice with 20-mL portions of DMF, three times with 20-mL portions of THF, and three times with 20-mL portions of ethanol. The resulting orange beads were dried in an oven at 60 °C and stored in a glass vial under ambient conditions. Anal. found (200- μ m beads): C, 83.65; H, 7.29; N, 0.58. The low N content suggests that the reaction was only ca. 10% complete. IR (KBr): $\nu_{\text{N=N}}$ 1369 cm^{-1} ; $\nu_{\text{S=O}}$ 1180 and 1029 cm^{-1} .

Measurements of Charge. The beads of interest were placed in an aluminum dish with a diameter of 5 cm. A mechanical shaker shook the dish at approximately 10 Hz for at

least 5 minutes; the motion of the dish caused the beads to roll around in the dish. The same charge measurements were obtained whether the aluminum dish was grounded, insulated, or biased at either +10 kV or -10 kV with a high-voltage DC power supply (Spellman). The fact that the bead charge was insensitive to the electrical potential of the dish suggests that the charging of these beads is due to ion transfer and not electron transfer.

The charge on each bead was measured using the following apparatus: A polyethylene tube (2 mm diameter) was connected to a vacuum source and threaded through 3 concentric aluminum cylinders. The three concentric cylinders were approximately 4, 9, and 30 mm in diameter and 1.0, 1.1, and 1.4 meters in length, respectively. Concentric solid polyethylene tubing insulated the cylinders from each other. The three cylinders were soldered to the three leads of a triaxial shielded cable (Belden 9222), with the innermost cylinder connected to the central lead; these connections were all enclosed within the outermost shielding cylinder. This shielding configuration was necessary in order to make measurements with low noise (RMS noise ~ 20 fC) and minimal background drift. The triaxial cable was connected directly to a Keithley model 6514 electrometer in charge-measurement mode: in this mode, the instrument acts as a current integrator. The total charge (time integral of the current) was recorded 60 times per second on a computer connected to the electrometer.

In charge-measurement mode, the electrometer maintains the two innermost aluminum cylinders at the same electrical potential. The vacuum drew air through the central polyethylene tube. When the end of the tube was brought close to a small bead, the flow of air drew the bead into the tube. As the bead passed into the innermost metal cylinder, any charge on the bead induced on the cylinder an equal charge, which was detected by the electrometer. For instance, if a positive bead entered the cylinder, the electrometer reading would increase by an amount equal to the charge on the bead. Once the bead exited the cylinder, the induced charge vanished and the electrometer reading

would return, on average, to its initial value. Each positive bead thus gave an upward-pointing peak on the electrometer trace, while each negative bead gave a downward-pointing trough.

Each peak or trough was not exactly symmetrical: the charge on the bead when it entered the tube was not the same as the charge on the bead when it exited the tube. The flow of air in the tube is turbulent (Reynolds number ~ 6000), so the bead will inevitably collide with the walls of the tube. Presumably, contact electrification between the bead and the polyethylene tube changed the charge of the bead. The difference between those two charge measurements, however, was not statistically significant for either sample of beads. We measured the charges on 44 individual tetraalkylammonium beads (1) and 40 individual sulfonate beads (2). A paired t-test for the mean difference did not show statistical significance at a 95% confidence level, and the 95% confidence interval for the mean difference was, in both cases, smaller than the standard deviation of the bead charge. Nevertheless, we took the charge on each bead to be that measured as the bead entered the tube, in order to minimize any effects of interactions with the polyethylene.

We have studied the reproducibility of this charge-measuring device and will prepare a detailed report for a future publication. Briefly, we measured the charge on hundreds of beads under various ambient laboratory conditions and found that the mean charge measured by this device is reproducible to within about one standard deviation (ca. 25% of the mean charge).

Self-Assembly. The beads of interest were combined in an aluminum dish with a diameter of 5 cm. Typically, we combined large beads with one type of charge and smaller beads with the other charge. The dish was tapped with a metal spatula ca. 20-50 times until the beads were thoroughly mixed. Each large bead became coated with a monolayer of the oppositely-charged small beads. These assembled structures were then poured out of the dish. Experiments using a gold-coated glass dish and an aluminum dish

yielded indistinguishable results. Attempts at assembly in uncoated glass dishes or polystyrene Petri dishes were less successful: these electrically insulating surfaces appeared to develop local regions of charge—“hot spots”—on which the beads adhered.

For the multistep self-assembly experiments, the assembled structures from the first step were transferred to a clean aluminum dish, heated in an oven at ca. 260 °C for 10-15 minutes, and allowed to cool to room temperature. The next layer of beads was added to the annealed assemblies and the same process of self-assembly was performed.

Control Experiments. For the control experiments, 200- μm -diameter polystyrene beads and 20- μm -diameter polystyrene beads (Duke Scientific) were washed with water, DMF, THF, and ethanol according to the same protocol used for the functionalized beads, dried in an oven at 60°C, and stored in a glass vial under ambient conditions. These cleaned beads were combined in an aluminum dish and self-assembly was attempted following the protocol described above. Almost no adhesion was observed between these unfunctionalized beads, as shown in Figure S2. The large bead in the upper-right corner of that image has about 20 small beads adhered; most of the other large beads have two or fewer small beads adhered.

Electrostatic Calculations

We calculated the total electrostatic energy of a model system consisting of a single 200- μm -diameter sphere with a positive charge of +0.01 nC surrounded by 272 negatively-charged spheres, each with a diameter of 24 μm and a charge of -7.35×10^{-5} nC. For simplicity, we treated each sphere as a nonpolarizable hard sphere with a point charge at its center. The total charge on all the small spheres was equal to twice the charge on the large sphere, so the entire assembly had a total charge of -0.01 nC. The coordinates of the small spheres were taken from the database, “Minimal Energy Arrangements of Points on a Sphere” by R. H. Hardin, N. J. A. Sloane, and W. D. Smith.^[3] The total

electrostatic energy was calculated by summing the Coulombic energy for every pair of spheres in the structure. The attractive energy between a single small sphere and the large central sphere was -5.90×10^{-11} J, for a total attractive energy of -1.61×10^{-8} J. The mutual repulsive energy between all the small like-charged spheres was 1.50×10^{-8} J. The overall electrostatic energy (compared with the spheres separated from each other at an infinite distance) was -1.1×10^{-9} J. As long as the total charge on the small spheres was less than -0.0214 nC, the total electrostatic energy of this model assembly was negative. These calculations demonstrate that an assembly with an overall net electrostatic charge can be stable as a result of Coulombic interactions alone.

References

- [1] S. Itsuno, K. Uchikoshi, K. Ito, *J. Am. Chem. Soc.* **1990**, *112*, 8187.
- [2] *Biochemical Preparations, Vol. 1* (Ed.: H. E. Carter), Wiley, New York, **1949**, p. 17.
- [3] Available online at <http://www.research.att.com/~njas/electrons/index.html>
(Accessed 8/22/06).