

Contact de-Electrification of Electrostatically Charged Polymers

Supporting Information

Siowling Soh, Sen Wai Kwok, Helena Liu, and George M. Whitesides*

Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St. Cambridge,
MA 02138, U.S.A.

* To whom correspondence may be addressed: gwhitesides@gmwgroup.harvard.edu

1. Experimental Methods

Materials used for Charging Beads

The beads (1/4-inch in diameter, McMaster-Carr) used in the experiments were Nylon (polyamide 6/6), Delrin (polyoxymethylene), Teflon (polytetrafluoroethylene), and Torlon (polyamide-imide). A square aluminum dish with inner dimension of 8.8 cm (made in-house) held and constrained the beads within its boundary. Before the experiments, we rinsed the beads and dish with deionized water and ethanol, and dried them in a stream of nitrogen. All experiments were conducted in a pyramidal glove bag (Captair) under an atmosphere of nitrogen gas (unless otherwise specified) and at a relative humidity of $\sim 1 - 2\%$ (measured using a Hygrometer, from VWR). A linear motor (LinMot) agitated the aluminum dish containing the beads. All manual manipulation of the beads was carried out using pairs of polybutylene terephthalate tweezers (McMaster-Carr).

Charge Measurement Using a Faraday Cup

We made the Faraday Cup (in-house) for measuring charge out of two hollow metallic cubes (made of stainless steel sheets) with one cube (8 cm in length) placed inside another cube (10 cm in length), separated by insulating foam (Neoprene Foam with adhesive back, McMaster-Carr). The inner cube was connected to an electrometer (Keithley 6514), while the outer cube was grounded. In order to facilitate placing the beads into the Faraday Cup, we cut a small hole (2 cm in diameter) on a top surface of the Faraday Cup. Any charged object dropped into the Faraday Cup induced an equal amount of charge with opposite polarity in the inner cube. In the electrometer, the amount of induced charge, Q , stored in a capacitor, with capacitance, C could

be calculated by the equation $Q = CV$, by measuring the potential difference, V , across the capacitor.¹ The electrometer displayed the resulting charge as a digital readout.

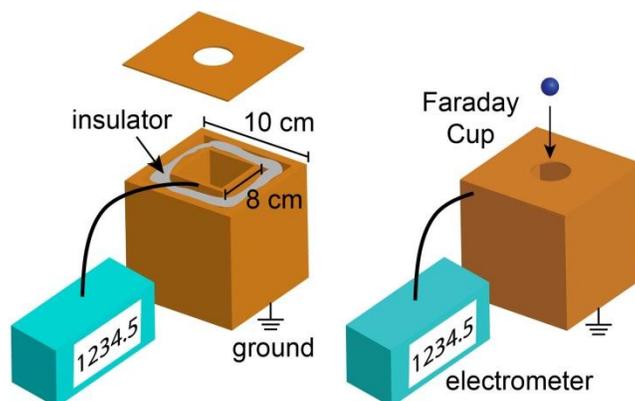


Figure S1. Illustration of the Faraday Cup connected to an electrometer

Procedure for Charging Beads

To charge polymeric beads, we arranged nine beads with an excess number (199) of oppositely-charged beads on an aluminum dish (a relatively non-charging surface according to the triboelectric series). Specifically, we packed the square dish (16 rows and 13 columns of beads in hexagonal structure) with nine beads of the desired material in the dish evenly spaced and surrounded only by oppositely-charging beads (see Figure 2 in the main text, top scheme, for an illustration). This arrangement ensured that the beads were confined to a location and not free to move across the dish, while providing sufficient space for the beads to rotate and collide with their neighboring beads. The combinations of beads used were as follows: Nylon beads with an excess Teflon beads, Teflon beads with an excess Nylon beads, Delrin beads with an excess Teflon beads, and Torlon beads with an excess Delrin beads. These combinations of charging generated high initial charges ($\sim\pm 20 \mu\text{C}/\text{m}^2$, see Figure 3) of the beads. We agitated the combination of beads linearly on the dish for 3 mins at an amplitude of 9 mm at 6 Hz.

Materials used for Discharging Beads

The top substrate was a hollow cube (Electron Microscopy Sciences) made of polystyrene with one of its external surfaces covered with double-sided tape (3M). The bottom substrate consisted of three layers of PMMA slabs ($2.5\text{ cm} \times 2.5\text{ cm} \times 1\text{ mm}$). We cut out five pockets in each PMMA slab as shown in Figure S2 with a Laser cutter (VersaLASER, model no. VLS 3.50, Universal Laser Systems), and taped the three slabs together.

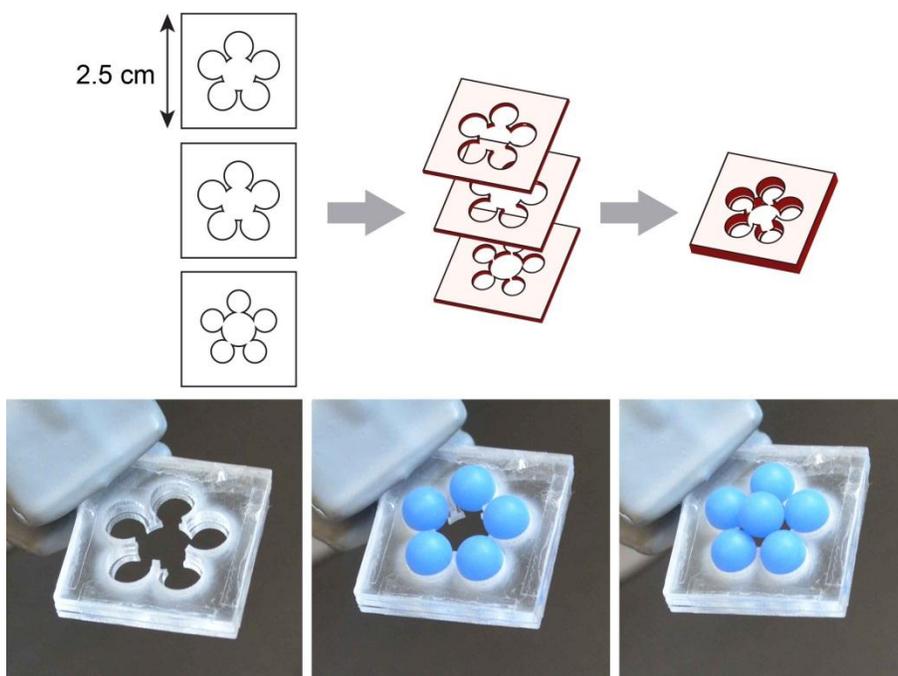


Figure S2. The scheme shows the dimension and the fabrication of the PMMA bottom substrate. Three pieces of PMMA slabs were cut to the geometries as illustrated in the scheme on the left using a Laser cutter. The bottom piece had slightly smaller pockets than the top two pieces (which are identical). The three pieces were taped together, forming the holder for the beads to rest on. The smaller pockets on the bottom piece enabled the beads to rest on the bottom piece and not fall through the holes of the pockets. The bottom images are photographs of the PMMA

substrate, without any beads (left), with five side beads (middle), and with a center bead placed in between and on top of the five side beads (right). The beads were 1/4 inch in diameter.

Procedure for Discharging Beads

After charging, we placed five charged beads (side beads) in the pockets of the bottom PMMA substrate and a sixth bead (center bead) in the middle and on top of these five beads, so that the sixth bead was in contact with only other charged beads of the same material and not with any other solid substrate. A seventh bead (top bead) was placed on the top adhesive surface and was rubbed against the center bead. Since the bottom area of the center bead was not accessible for rubbing, we rotated the center bead with a pair of tweezers by $\sim 180^\circ$ in order for the entire surface of the center bead to be rubbed. The center bead was rotated in four different directions, each separated by 45° (Figure S3). The process was repeated so that the center bead was rotated eight times, with the process lasting ~ 3 mins. This procedure of rubbing the beads may be excessive: the center bead might discharge completely with lesser number of rubs and rotations, but this procedure ensured that the beads were always almost completely discharged.

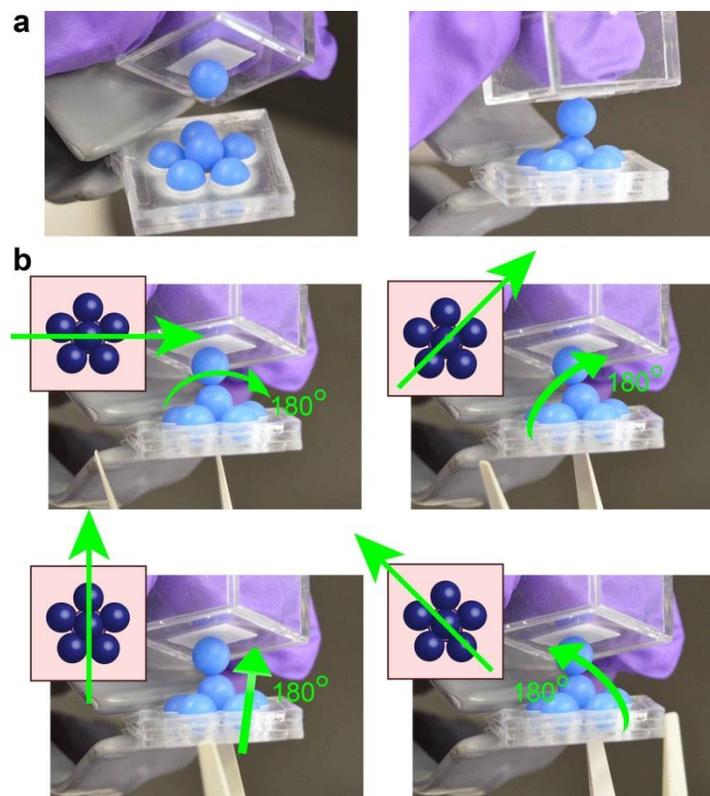


Figure S3. Procedure for discharging charged beads. (a) Images of five side beads placed in pockets of a bottom PMMA substrate, a center bead placed over the five beads, and a top bead adhered on a surface covered with double-sided tape (left). Discharge occurred when the top bead was brought into contact with the center bead (right). (b) The center bead was rotated by a pair of tweezers in four different directions; the top bead was rubbed against the center bead after each rotation. Arrow in the inset at the top left corner of each image indicates the direction along which the center was rotated. The center bead was rotated by 180° for each rotation.

2. Undyed Nylon Beads Discharge Similarly to Dyed Beads on Contact

In our experiments, in order to differentiate visually the colorless beads of different materials, we dyed the Nylon beads blue using disperse blue dye (Sigma-Aldrich). Control

experiment (same procedure as illustrated in Figure 2, main text) with undyed Nylon showed that the undyed Nylon beads discharged similarly to dyed beads (Figure S4).

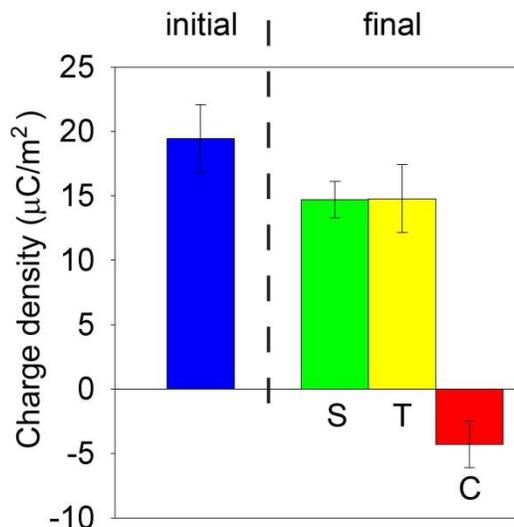


Figure S4. Undyed Nylon beads demonstrate similar behavior of contact de-electrification. After contact, the center bead discharged (S = side bead; T = top bead; C = center bead).

3. Alternative Experimental Setup for Contact de-Electrification

To show that charged beads are capable of complete discharge, the entire surfaces of the beads need to be brought into contact. Figure S5 illustrates an alternative experimental setup that also demonstrates contact de-electrification. Six charged Nylon beads immobilized within the interior of an adhesive container (polypropylene with double-sided tape, 3M) created a cavity in the middle of the container (see Figure S5 and caption for more details). A seventh charged Nylon bead (hereby referred to as the “mobile bead”) placed in the cavity, was surrounded by the other six like-charged beads — importantly, this bead was only in contact with like-charged beads and not in contact with any other solid substrates. After agitating the container linearly for

3 mins (at an amplitude of 9 mm at 6 Hz), we measured the charge on the mobile bead by a Faraday cup. Results (Figure S5b) show that the mobile bead discharged after agitation. We performed a control experiment by holding charged beads with a pair of tweezers and manually agitating them in air for 3 mins; the beads did not discharge.

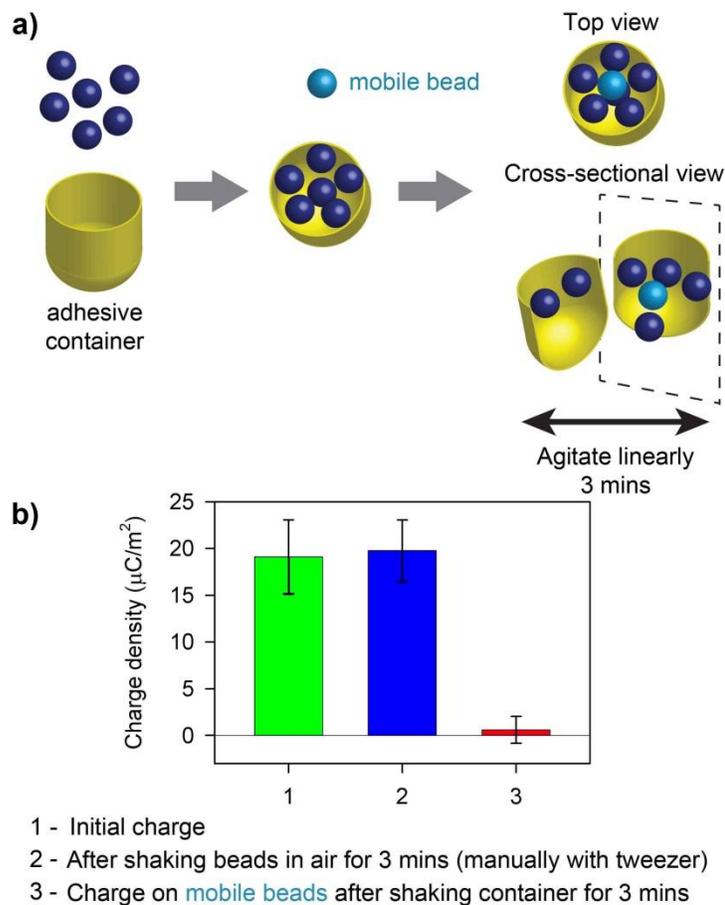


Figure S5 An alternate experimental setup for observing contact de-electrification. (a) Six already-charged Nylon beads were placed in a container with adhesive interior, so that they were fixed in position. The first bead was placed at the bottom of the container, whereas the five other beads were fixed above the first bead and onto the sides of the container, arranged in a pentagon. A seventh Nylon bead (the “mobile bead”, colored light blue for clarity) was inserted loosely in

the cavity formed by the six beads, where it rested on top of the bead at the bottom of the container and against some of the beads on the sides. When the container was agitated, the mobile bead jiggled and knocked against the other six beads held in position by double-sided tape on the interior wall of the container. (b) Charge measurement ($n = 12$) showed that the mobile bead discharged almost completely after agitation. Another experiment was done ($n = 6$) in which an already-charged bead was held by a pair of tweezers manually and was shaken vigorously in air for 3 mins — the bead did not discharge.

4. Dependence of Dielectric Breakdown Strength on Composition of the Gaseous Atmosphere

When polymeric beads are charged by contact electrification (see Figure 2 top scheme for the charging procedure), the charge of the bead at steady-state depends on the dielectric breakdown strength of the gaseous atmosphere surrounding the beads. Instead of using a single type of gas, it is also possible to purge the glove bag with a mixture of gases. For the case of a mixture of two gases, the dielectric breakdown strength of the mixture lies in between the dielectric breakdown strengths of the pure gases (Figure S6). The steady-state charge on the beads after charging should, therefore, follow qualitatively similar trends as the dielectric breakdown strength of gases with respect to the composition of the gases.

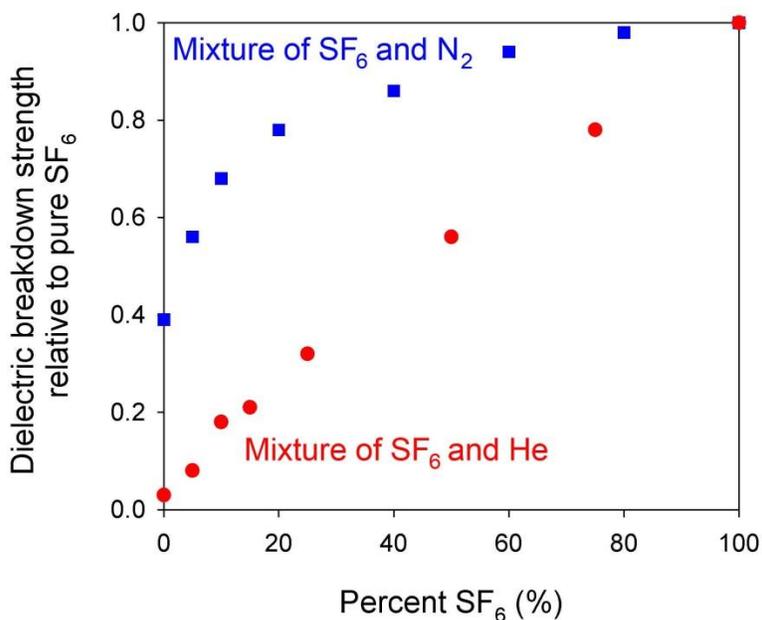


Figure S6. Dielectric breakdown strength of a mixture of sulfur hexafluoride (SF₆) and nitrogen (N₂) or helium (He). (Data taken from Table 6.11 of ref ²)

5. Charge Did Not Transfer via the PMMA Dish to Other Solid Substrates

The experiment conducted in Figure 6 of the main text indicated that charge was transferred to the gaseous atmosphere. Although charges might also transfer from the charged beads to the inner surface (especially bottom) of the PMMA dish, it was practically impossible for these charges to penetrate through the bottom of the insulating dish (3 mm thick) to the aluminum foil underneath. Previous studies of charges deposited on surfaces of polymers (e.g. using pulses of electron beams at a few kV) showed penetration depths into the bulk polymer on the order of a few nanometers up to a few microns at most.³⁻⁵ Lateral migration of charges across the polymeric surface is also not possible within the timeframe of our experiments⁶; some studies even made use of the fact that charges are stationary for nanopatterning of charges on PMMA

surface.^{7,8} Furthermore, our experiments in Figure 5 showed that the bottom PMMA substrate did not accumulate charge when in contact with charged beads.

References for Supporting Information:

- (1) Wiles, J. A.; Grzybowski, B. A.; Winkleman, A.; Whitesides, G. M. *Anal. Chem.* **2003**, *75*, 4859-4867.
- (2) Slade, P. G. *The Vacuum Interrupter: Theory, Design, and Application*; CRC Press: Boca Raton, 2008.
- (3) Watson, P. K.; Yu, Z. Z. *J. Electrostat.* **1997**, *40-1*, 67-72.
- (4) Lowell, J.; Roseinnes, A. C. *Adv. Phys.* **1980**, *29*, 947-1023.
- (5) Burkett, S. L.; Charlson, E. M.; Charlson, E. J.; Yasuda, H. K. *J. Appl. Polym. Sci.* **1996**, *61*, 47-56.
- (6) Baytekin, H. T.; Patashinski, A. Z.; Branicki, M.; Baytekin, B.; Soh, S.; Grzybowski, B. *A. Science* **2011**, *333*, 308-312.
- (7) Ressler, L.; Le Nader, V. *Nanotechnology* **2008**, *19*, 135301.
- (8) Seemann, L.; Stemmer, A.; Naujoks, N. *Microelectron. Eng.* **2007**, *84*, 1423-1426.