

## Supporting Information

### **Non-close-packed arrangement of soft elastomer microspheres on solid substrates**

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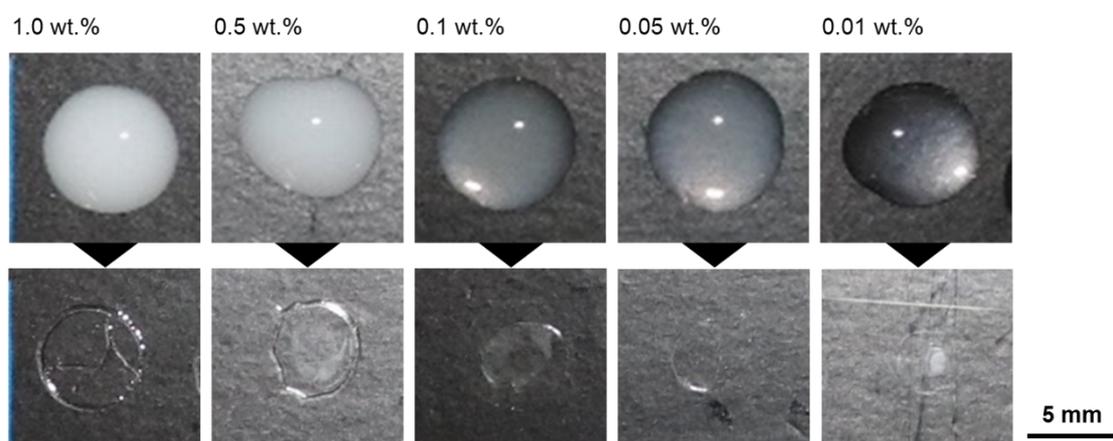
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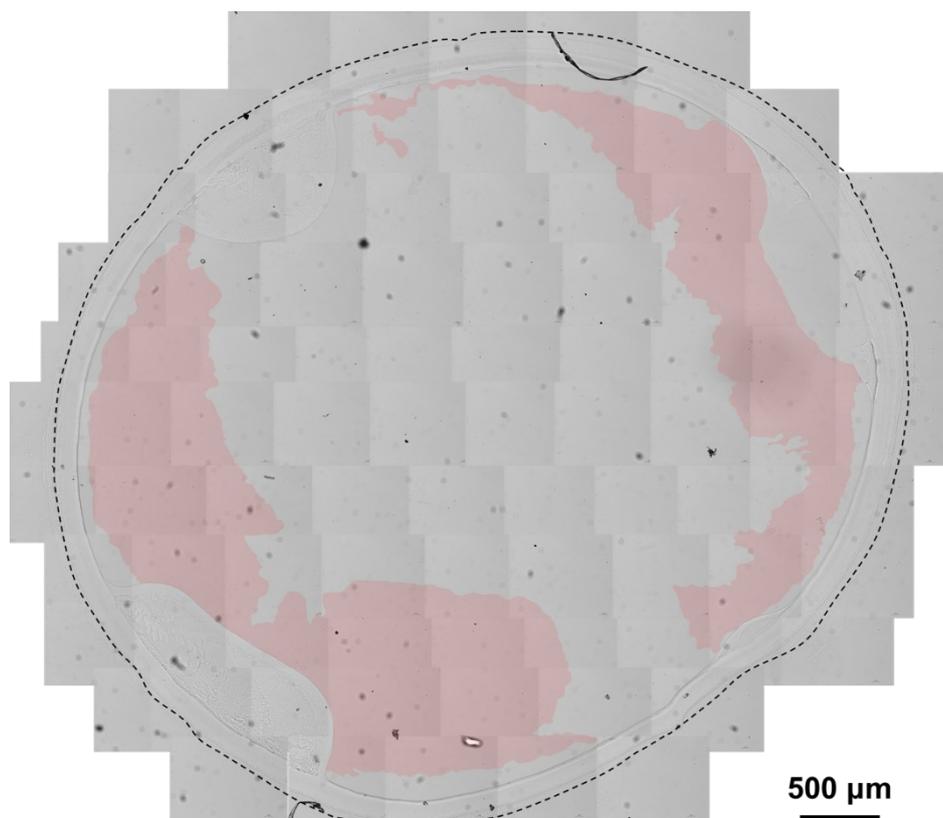
## Results and Discussion

**Table S1.** Chemical composition, hydrodynamic diameter  $D_h$ , and zeta potential of the elastomer pBA and pEA microspheres prepared by surfactant-free emulsion polymerization.

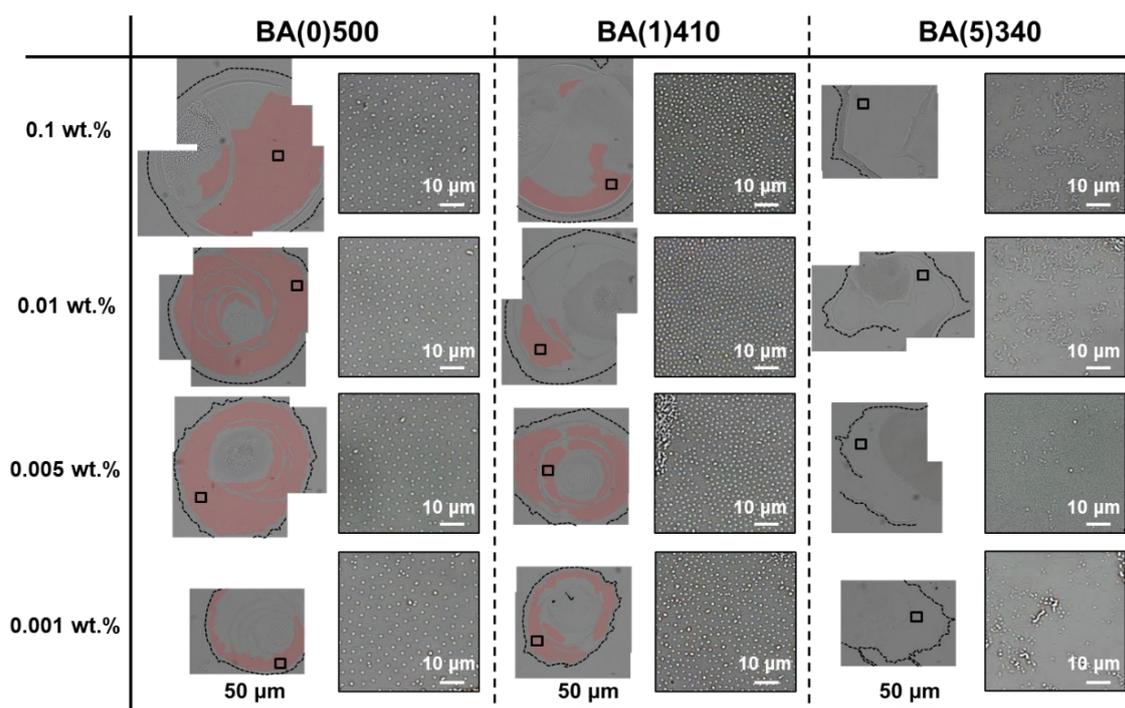
Code	EA [mol.%] (g)	BA [mol.%] (g)	DVB [mol.%] (g)	Monomer conc. [mM]	Water [g]	$D_h$ [nm]	Zeta potential [mV]
BA(0)500	0	100 (19.2 g)	0	1500	100	498	-32.7
BA(0)710	0	100 (96.1 g)	0	1500	500	711	-40.5
EA(0)260	100 (5.0 g)	0	0	500	100	256	-24.3
EA(0)390	100 (15.0 g)	0	0	1500	100	393	-23.9
EA(0)710	100 (30.0 g)	0	0	3000	100	707	-39.4
BA(1)410	0	99 (95.1 g)	1 (0.98 g)	1500	500	409	-35.6
EA(1)450	99 (74.3 g)	0	1 (0.98 g)	1500	500	454	-44.7
BA(5)340	0	95 (30.4 g)	5 (1.63 g)	500	500	337	-42.7



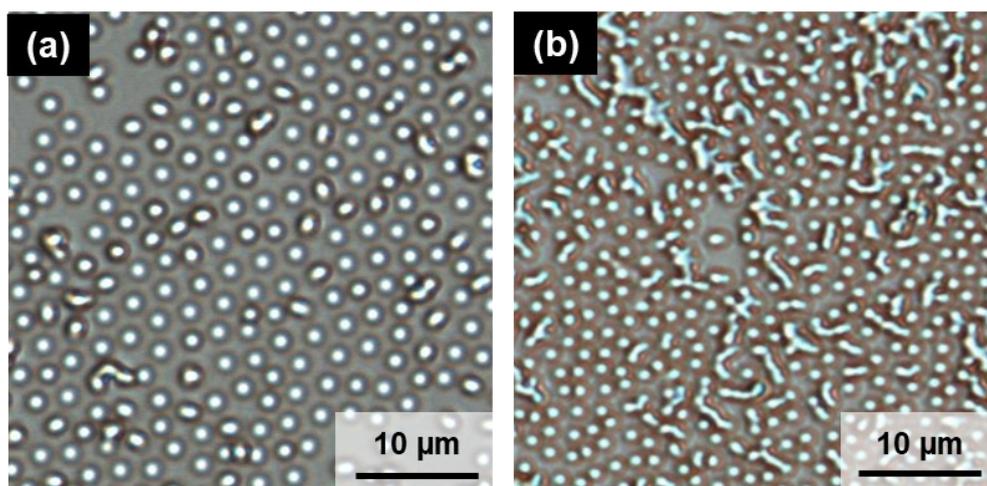
**Figure S1.** Photographs of sessile droplets and dried thin films containing BA(0)710 microspheres formed by drying 30  $\mu$ L droplets of dispersions with different particle concentrations on glass substrates at room temperature ( $\sim 25$   $^{\circ}$ C,  $\sim 30\%$  humidity).



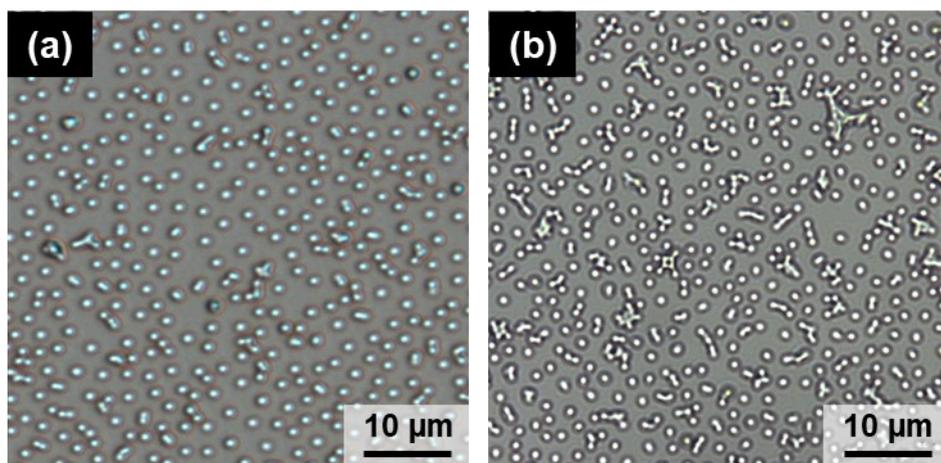
**Figure S2.** Optical microscopy image of BA(0)710 microspheres on a glass substrate after drying a sessile droplet of the dispersion (30  $\mu\text{L}$ ,  $\sim 25^\circ\text{C}$ ,  $\sim 30\%$  humidity). Note that this image was formed by overlaying multiple images to observe the whole droplet. Dotted lines show the edges of the film. The areas marked in red represent the regions where a non-close-packed ordered structure was observed.



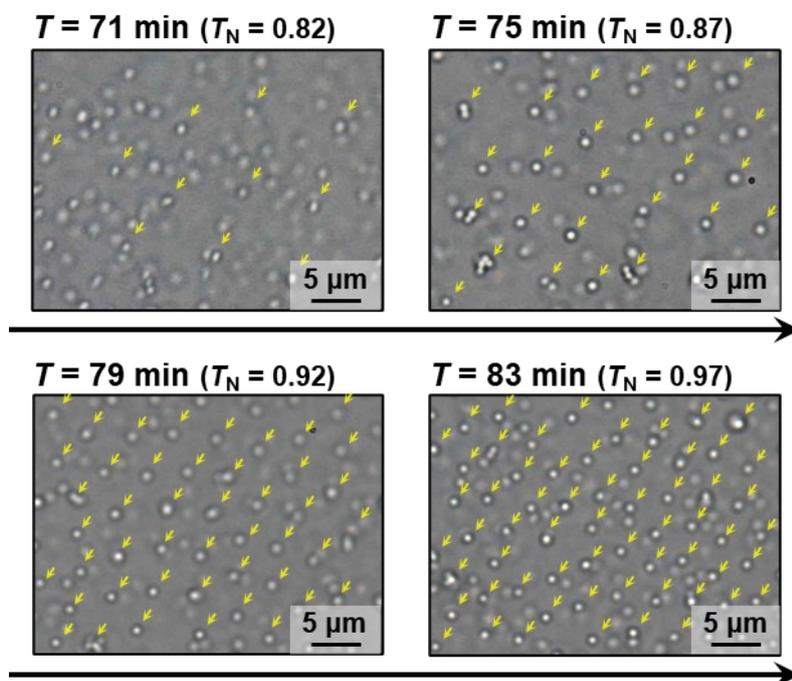
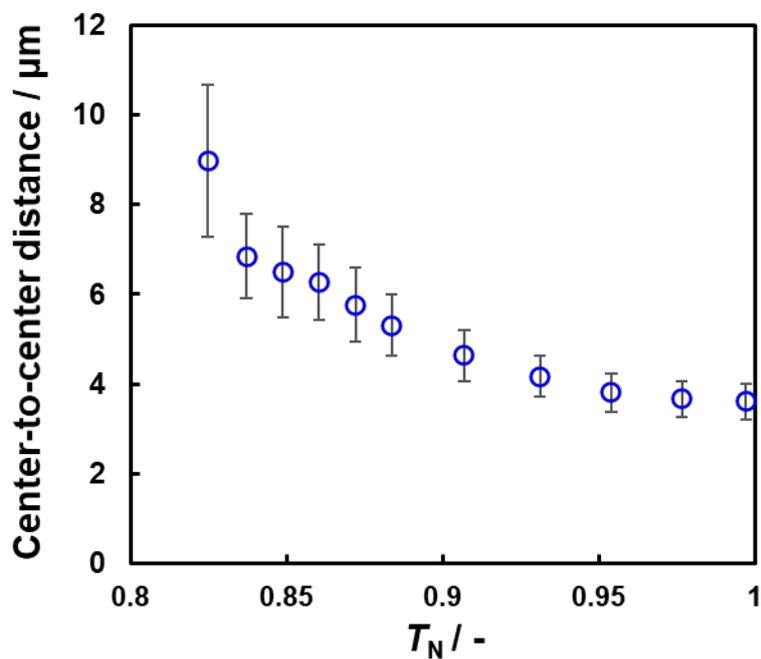
**Figure S3.** Optical microscopy images of BA(0)500, BA(1)410, and BA(5)340 microspheres on glass substrates after drying sessile droplets of their dispersions (1  $\mu\text{L}$ ,  $\sim 25^\circ\text{C}$ ,  $\sim 30\%$  humidity). Note that these images were formed by overlaying multiple images to observe the whole droplet. Dotted lines show the edges of the films. The areas marked in red represent the regions where a non-close-packed ordered structure was observed. The optical images shown at the right for each film are expansions of the regions indicated by black squares in the left-hand images.



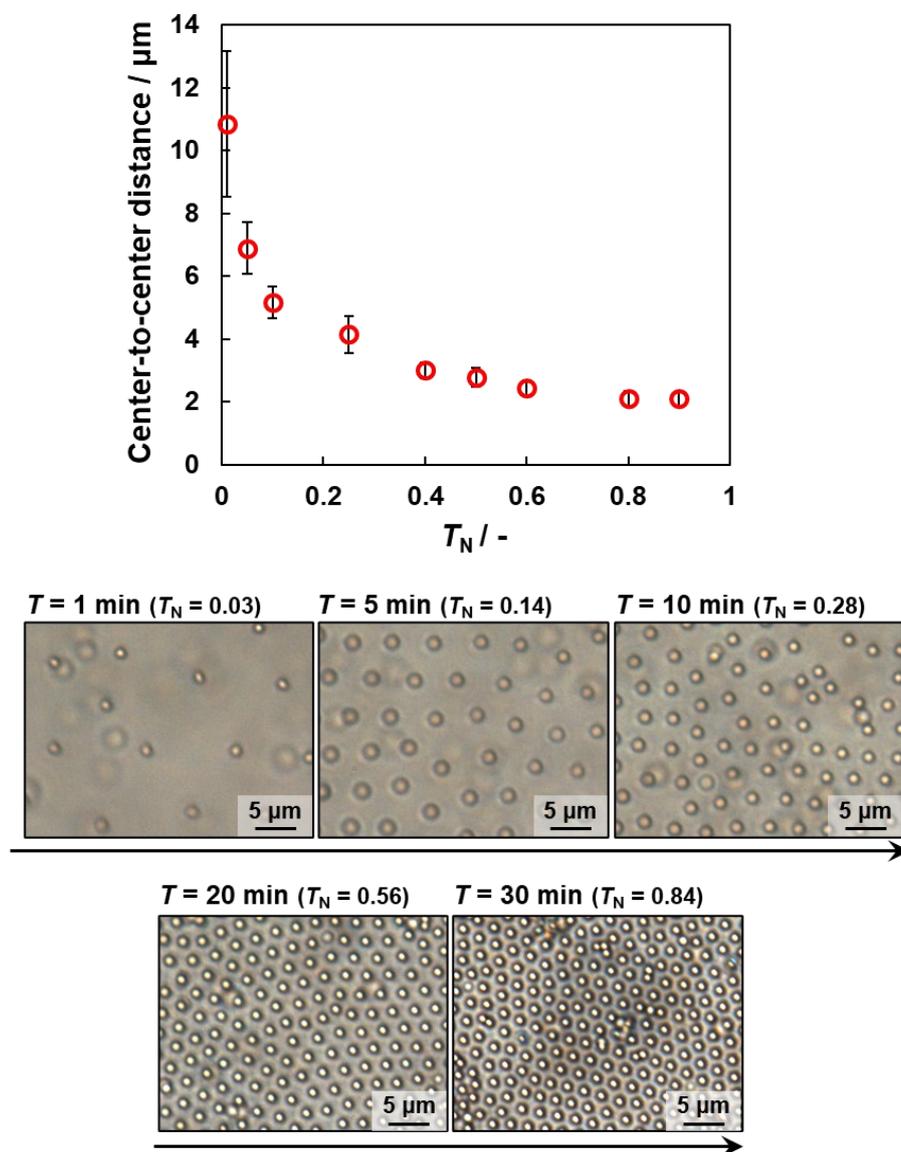
**Figure S4.** (a) Representative optical-microscopy image of the dried structure of the EA(0)710 dispersion (0.1 wt.%, 1  $\mu\text{L}$ ) on the glass substrate. (b) Representative optical-microscopy image of the dried structure of the EA(0)710 dispersion (0.1 wt.%, 3  $\mu\text{L}$ ) on a polystyrene (PS) substrate (Iwaki, 60 mm/Non-Treated Dish, Asahi Glass Co., Ltd.; prior to the experiment, the substrate was cleaned with detergent in water, followed by washing with pure water.)



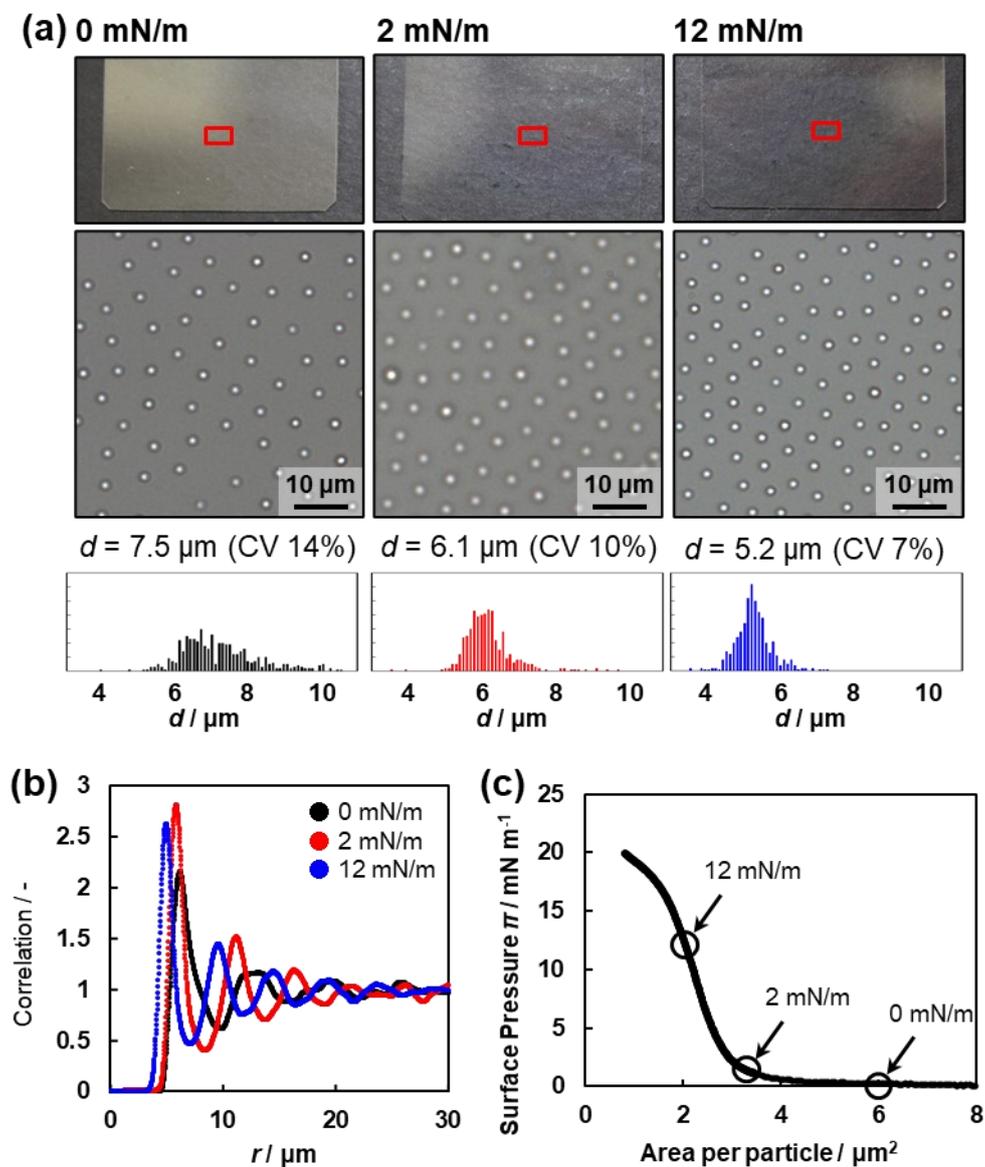
**Figure S5.** Optical-microscopy images of dried structures of EA(0)710 dispersions (0.01 wt.%) with different salt (NaCl) concentration on glass substrates: **(a)** 10 mM, **(b)** 30 mM. A uniform non-close-packed structure was obtained after drying dispersions at 10 mM as shown in **(a)**. Further addition of salt (30 mM), the microspheres aggregated in the bulk or at the air/water interface during the drying process and the drying structure was not ordered as shown in **(b)**; this is possibly due to a decrease of the electrostatic stability of the microspheres that results from the increasing salt concentrations upon evaporation of water.



**Figure S6.** Time dependence of the center-to-center distance of EA(0)710 microspheres (0.05 wt.%, 10  $\mu\text{L}$ ) adsorbed at the air/water interface during drying on a glass substrate at  $\sim 25$   $^{\circ}\text{C}$  ( $\sim 30\%$  humidity) ( $N = 50$  at  $T_N = 0.82$ ;  $N = 200$  at  $T_N = 0.83 \sim 1$ ). The microspheres adsorbed at the air/water interface are indicated by yellow arrows.



**Figure S7.** Time dependence of center-to-center distance of PS microspheres (0.08 wt.%, 1  $\mu\text{L}$ ) adsorbed at the air/water interface during drying on a glass substrate at  $\sim 25$   $^{\circ}\text{C}$  ( $\sim 30\%$  humidity) ( $N = 50$  at  $T_N = 0.01$ ;  $N = 200$  at  $T_N = 0.05 \sim 0.9$ ).



**Figure S8.** (a) Photographs and optical microscopy images of thin films obtained via the Langmuir–Blodgett method at surface pressures of 0 mN/m, 2 mN/m, and 12 mN/m. Note that the thin film prepared at 0 mN/m after compression at the interface until 2 mN/m. (b) Pair correlation functions of the arrays on the glass substrate obtained via the Langmuir–Blodgett method at the different surface pressures. (c) Surface pressure–area curve of the EA(0)710 particles obtained by means of the Langmuir–Blodgett method. A 0.2 wt% elastomer microsphere dispersion (1000  $\mu\text{L}$ ) was mixed with the same volume of ethanol and cast onto the air/water interface.

**Movie S1.** Moment during the evaporation of water when the EA(0)710 microspheres adsorbed at the air/water interface were transferred on a glass substrate.

**Movie S2.** Moment during the evaporation of water when the PS microspheres adsorbed at the air/water interface were transferred on a glass substrate.