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Electronic Supplementary Information

Photolithographically Assembled Polyelectrolyte Complexes as Shape-Directing Templates for Thermoreversible Gels

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A. Confirming the Removal of the Sacrificial PEC Template

To confirm that the PECs were successfully removed from the gels after their wash in 3.5 M NaCl solution, PEC-templated, toroid-shaped agarose gels (see Fig. 2a) were first placed in 10 mL of 0.06 M HCl solutions overnight while stirring at 400 rpm (to dissolve any residual PECs; see Ref. 53). To dissolve the agarose, the mixtures were then heated in an 80 °C water bath for 30 min while stirring at 120 rpm. Upon cooling to room temperature, the agarose concentration was no longer high enough for gels to reform, which caused the residual polyelectrolyte molecules (and the agarose) to remain uniformly dissolved throughout the samples. These mixtures, which started out at a low pH of ~1.5, were then titrated with 0.1 M NaOH to investigate the changes in light scattering from these solutions with pH – i.e., as the pH was raised enough to allow insoluble PECs to reform as colloidal dispersions, the presence of remaining polyelectrolyte was revealed by increased light scattering. The evolution in pH was monitored using a Mettler-Toledo (Columbus, OH) pH meter equipped with an InLab Expert Pro electrode. The light scattering intensities from these mixtures, on the other hand, were quantified using a Zetasizer Nano ZS (Malvern, UK) dynamic and electrophoretic light scattering instrument and compared with control samples prepared from PEC-templated gels that still contained their parent PECs (i.e., control samples that were not subjected to the PEC-removing salt wash).

Initially, at pH 2 (see Fig. S1), the light scattering was comparable to a particle-free solution, regardless of whether the PECs were washed out of the agarose gels. This was because PAA was largely protonated and therefore unable to form ionic (PEC) bonds with the PAH. As the pH was raised, however, the scattering intensity for mixtures prepared from gels where the PECs were not dissolved and washed away increased drastically (Fig. S1). This increased light scattering intensity (despite some fluctuations in its magnitude) persisted over a pH range of 2 – 10, regardless

of whether the agarose rings were formed using 0.5 or 2.0 wt% agarose solution (cf. Fig. S1a and b). Above a pH of 10, however, the PAH amine groups became deprotonated (and thus neutralized) and the insoluble PECs ceased forming again. For mixtures prepared from gels subjected to the NaCl wash, on the other hand, the light scattering intensity remained around baseline levels across the entire experimental pH range (for both agarose concentrations; Fig. S1a and b), indicating that the polyelectrolyte was successfully removed by the washing procedure.

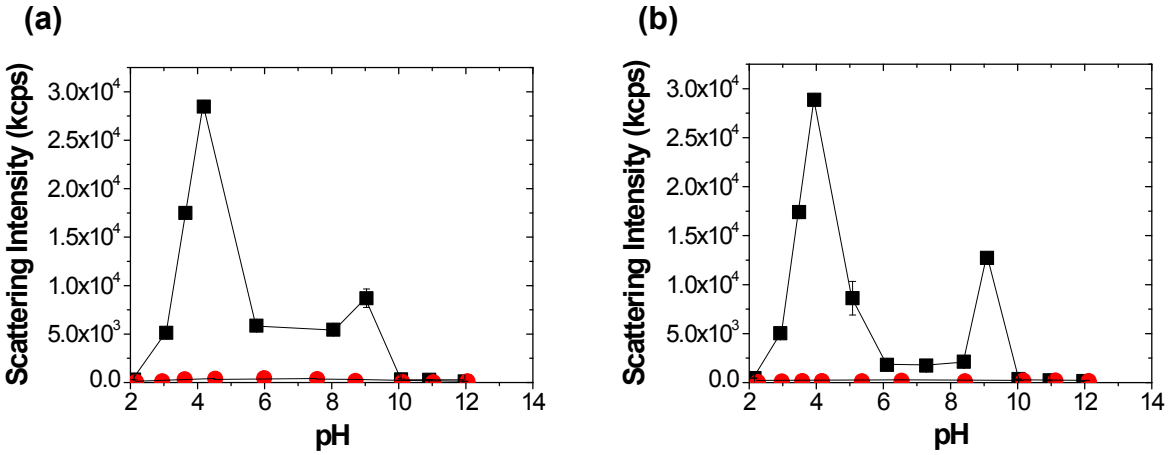

Fig. S1. Variation in light scattering intensity with pH for mixtures prepared from gels where the PECs (●) were removed via the NaCl wash and (■) where the PECs were not removed. These experiments were performed using both (a) 0.5 wt% and (b) 2.0 wt% agarose concentrations during the photolithographic assembly step. The error bars are standard deviations while the lines are guides to the eye.

B. Supplementary Rheology Data Comparing the Storage and Loss Moduli

Further rheology data comparing the storage (*G'*) and loss moduli (*G"*) of the PEC-templated gels (prepared using different, 0.5 – 2.0 wt% initial agarose concentrations) is provided in Fig. S2. At each concentration, the *G'*-values consistently exceeded the *G"*-values, thus confirming gel-like network properties. Like the data in Fig. 3, these frequency sweep measurements were obtained using the procedure in Section 2.4.

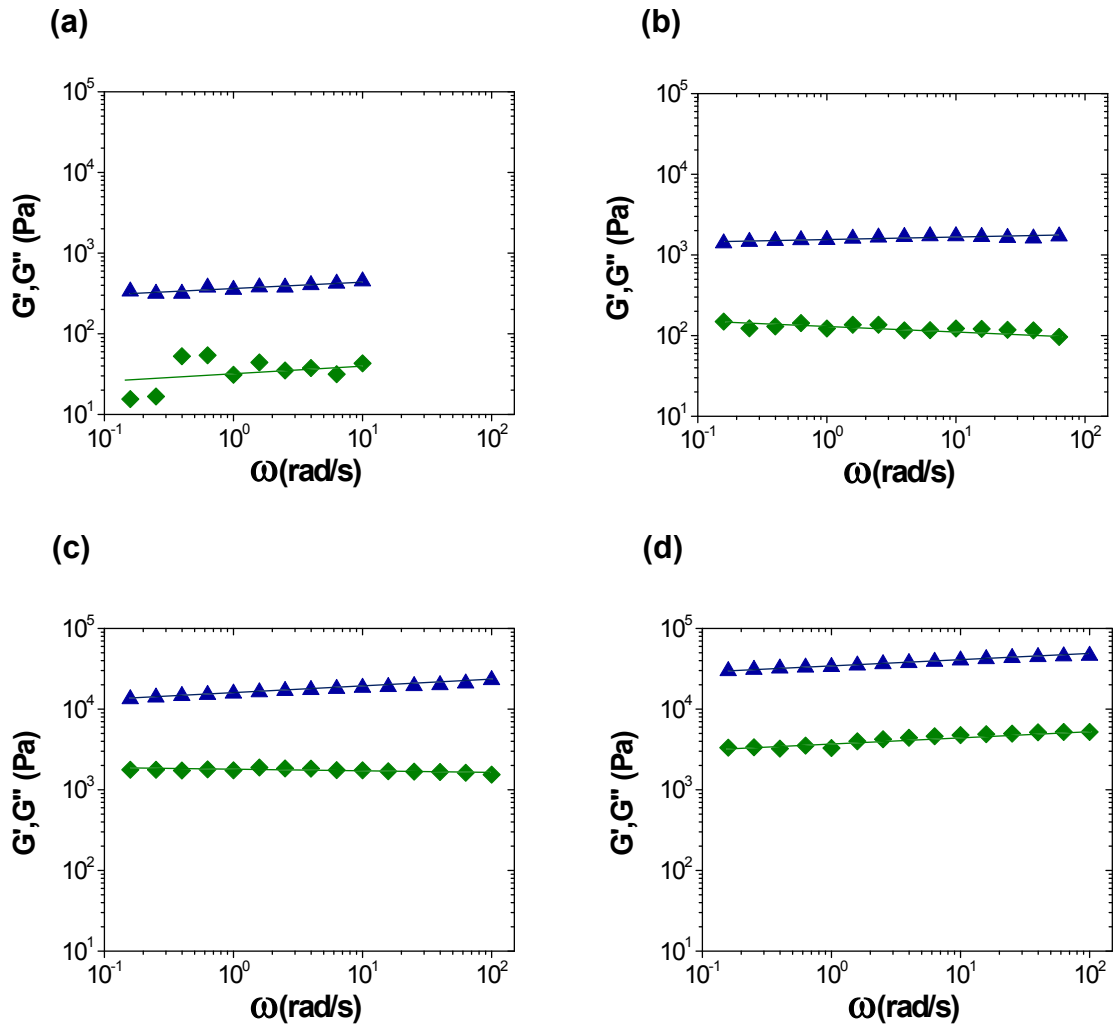

Fig. S2. Representative frequency sweep data showing the (□) storage moduli (*G'*) and (◆) loss moduli (*G"*) as functions of oscillation frequency (ω) for gels prepared using (a) 0.5 wt%, (b) 1.0 wt%, (c) 1.5 wt% and (d) 2.0 wt% agarose. The lines are guides to the eye.

C. Sample Preparation for Investigating PEC-Templated Assembly Effects on Gel Stiffness

To compare the stiffness of PEC-templated agarose gels with those formed using the standard preparation procedure (i.e., via simple gelation inside a mold), their dynamic rheology was probed. Regular (non-templated) agarose gels were prepared by first dissolving variously concentrated (0.5 – 2.0 wt%) agarose powder dispersions in water (by heating them in an 80 °C

water bath for 20 min while stirring at 120 rpm). The solutions were then poured into chambered microscope slides (as described in Section 2.3) and turned into gels by allowing them to cool; first, for 20 min at room temperature and, then, at 12 °C for an additional 10 min. The gels were then cut into 1 cm × 1 cm × 0.1 cm pieces with a razor. Finally, to expose these non-templated gels to the same salt concentrations as their PEC-templated counterparts, these gels were washed in 3.5 M NaCl solutions for 2 d, whereupon the NaCl solutions were diluted to an ambient NaCl concentration of 0.15 M with 10 mM (pH 7) sodium phosphate buffer solution. The dynamic rheology of these gels was then characterized using the procedure described in Section 2.4.