Experimental Procedures

Monomer Synthesis. 2-(methacryloyloxy)ethyl phosphate (MOEP) was synthesized by adding phosphorus oxychloride (16.8g, 110 mmol) under argon to a stirred solution of 2-hydroxyethyl methacrylate (12g, 92 mmol) in toluene (340 ml). The reaction mixture was cooled to 0°C and triethylamine (39 ml, 276 mmol) was added. The reaction proceeded at 0°C for 30 mins, then at room temperature for 6 hrs. The white solid precipitate was recovered by filtration. Water (240 ml) was added to the filtrate and stirred overnight. The two layers were separated and the aqueous phase acidified, then extracted with THF: Ether (1:2, 6×225 ml). The organic phases were combined, dried over Na_2SO_4, and solvent evaporated to obtain the product as a pale yellow oil (67%, 12.2g). ^{1}H NMR spectroscopy (300 MHz, D_2O) d 1.7 (3H, s), 4.0 (2H, m, POC*H*$_2$), 4.2 (2H, m, $POCH_2CH_2$), 5.5 (1H,s) 6.0 (1H, s); ^{13}C NMR (75 MHz, D_2O) d 17.4, 64.2 (d, $^{2}J_{POC}$ = 8.3 Hz), 64.4 (d, $^{3}J_{POCC}$ = 5.5Hz), 127.2, 135.6, 169.4; ^{31}P NMR (120 MHz, D_2O) d 0.97 (s). Dopamine methacrylamide (DMA) was synthesized as previously described [4].

Co-polyelectrolyte synthesis. Poly(MOEP-co-DMA) was synthesized as previously described [4] by free radical polymerization of MOEP and DMA initiated with AIBN (Polysciences) in methanol. The polymerization proceeded at 60^{o}C for 24 hrs. The copolymer was precipitated with acetone then washed twice with acetone to remove residual monomers. The polymer was then dissolved in water and ultra-filtered on Pellicon Ultracel membranes (Millipore) with MWCO 1000 kDa followed by filtration with MWCO of 5 kDa. The concentrations of phosphate and *o*-DHP sidechains were

determined by NMR and UV/vis spectroscopy and were 76 and 19 mol%, respectively. The MW (64 kDa) and PDI (2.8) of the copolymer were determined by size exclusion chromatography (SEC) on an AKTA FPLC system with a Superose 6 HR 10/300 column (GE Healthcare) in 0.05 M phosphate and 0.15 M NaCl (pH 7.4).

Poly(acrylamide-co-aminopropyl methacrylamide) was synthesized by free radical polymerization of 90 mol% acrylamide (Polysciences) and 10 mol% N-(3-amino-propyl) methacrylamide hydrochloride (Polysciences) as previously described [4]. The copolymer was purified by dialysis for three days and lyophilized. The amine concentration (mol/mg) was determined with ninhydrin using glycine as the standard. The MW and PDI, determined by SEC in 0.5 M NaCl and 0.1 M $NH_4CH_3CO_2$ on Superdex 200 column (GE Healthcare), were 288 kDa and PDI 1.36.

Coacervate formation. PEG-dA (760 Da, Aldrich) was dissolved in degassed DI water at the desired concentration (0-25 wt%). Poly(acrylamide-co-aminopropyl methacrylamide) and poly(MOEP-co-DMA) were dissolved in separate PEG-dA solutions at final concentration of 5 wt%. The poly(MOEP-co-DMA) PEG-dA solution also contained a 0.2 molar ratio of Ca^{2+} to phosphate sidechains. The copolymer solutions were adjusted to pH 7.4±0.2 with NaOH. The poly(acrylamide-co-aminopropyl methacrylamide) PEG-dA solution was added dropwise while stirring to the poly(MOEP-co-DMA) PEG-dA solution to a molar ratio of 0.6 amine sidechains to phosphate sidechains. Within a few minutes a turbid coacervate settled out of solution.

Mechanical testing. The adhesive PEG-dA filled coacervates were crosslinked through the *o*-DHP sidechains of the polyphosphate and/or by polymerizing PEG-dA. *o*-DHP was oxidatively crosslinked by adding 1 equivalent of $NaIO_4$. To slow the oxidation of *o*-DHP sidechains to allow better control of the setting reaction, a sugar (1,2-O-Isopropylidene-D-glucofuranose, 98%) molecule is used to prepare an aqueous $NaIO_4$/sugar complex solution (100 mg/ml) with a $NaIO_4$: Sugar of 1:1.2 dissolved in water. PEG-dA was polymerized with 3.5 mol% ammonium persulfate (APS) and 5.2 mol% N,N,N',N'-tetramethylethylenediamine (TEMED). Immediately after adding $NaIO_4$, APS, and TEMED, 20 μl of coacervate was added to a wet 0.5 x 5 cm cleaned and polished Al adherend. A second wet Al was placed on the first with a 14-20 mm overlap, secured with a stainless steel clip, and submerged in water for 20-24 hrs at 22-24ºC. For each test condition 4-6 specimens were prepared. The shear strength of the bonds were determined on a material testing system (Instron) with a 500 N load cell, crosshead speed 0.2 mm min^{-1}, while fully submerged in a temperature controlled water bath.

Dynamic rheology. Flow experiments were done on a stress-controlled rheometer (TA Instrument, AR 2000ex) using a 20 mm, 4°cone and plate, gap 114 μm, at 25°C with 150 μL coacervate samples. All rheology experiments were repeated with three independently prepared coacervate samples.

ATR-FTIR. Attenuated Total Reflectance-Fourier Transform Infrared Microscopy (ATR-FTIR, FTS 6000 Spectrometer BioRAD) was used to measure the amount of PEG-dA in coacervates as well as the conversion of polymerization. The scans were made on ZnSe reflective crystal by placing 50 μl of coacervate and running 30 scans per spectrum. Standard PEG-dA solutions of known concentration in water were scanned to get a standard curve. Peak 1415 cm^{-1}, corresponding to the acrylate group in PEG-dA, was used to fit a linear model of Normalized peak area vs. known concentration. This standard curve fit was used to analyze the amount of PEG-DA in coacervates. Each sample was measured three times to get an average value.