**Fig. S1.** (a) The calibration curve constructed using the ratio of integrated FTIR intensities in the \( \text{\textgreater C=O} \) stretching region of PMAA_{150} (sum of 1700 and 1730 cm\(^{-1}\) bands) to that of -C-O-C-stretching vibrations of F127 (sum of 1070 and 1104 cm\(^{-1}\) bands) measured in the polymer mixtures with known compositions. (b) FTIR spectra of PMAA_{150}/F127 complexes precipitated from solutions at various mass ratios.
Fig. S2. (a) Hydrodynamic diameters of PMAA$_{80}$/F127 complexes with different ratios of components as a function of temperature. (b) The phase diagram of PMAA$_{80}$/F127 complexes in solutions at pH 2. Concentration of F127 was 0.5 wt%.

Fig. S3. DLS measurements in PMAA$_{150}$/F127 solutions of various compositions prepared using different mixing paths at 25 °C (a–d), or using the same mixing path, but different temperatures (e,f). The blue dotted line indicates the cutoff in the PEC sizes above which extensive PEC precipitation occurred.
**Fig. S4.** (a) Reversibility and hysteresis in hydrodynamic sizes measured in PAA$_{450}$/F127 0.25/1 solutions upon sequential heating and cooling using 10-min equilibration at each temperature. (b) Response of hydrodynamic diameters of PAA$_{450}$/F127 0.25/1 complexes to temperature variations. The insets are images of the PEC solution exposed to different temperatures.

**Fig. S5.** Time evolution of hydrodynamic diameters of PAA$_{450}$/F127 complexes of various compositions at different temperatures.
Fig. S6. Hydrodynamic diameters of PAA_{450}/F127 complexes prepared using different mixing paths at 25 °C (a), or using the same mixing path at different temperatures (b).

Fig. S7. Calibration curve constructed using PAA_{450}/F127 polymer mixtures with known mass ratios. The y axis shows the ratio of integrated intensities of absorption bands in the 1700 -1730 cm\(^{-1}\) region to those in the 1000 -1150 cm\(^{-1}\) region as determined by the curve fitting procedure shown in Fig. 5.
**Fig. S8.** Fluorescence spectra of pyrene obtained at the excitation wavelength of 332 nm with PMAA<sub>150</sub>/F127, PAA<sub>450</sub>/F127, PAA<sub>5</sub>/F127 and F127 solutions at pH 2. Concentration of F127 in all solutions was 0.5 wt%.

**Fig. S9.** FTIR spectra of F127 (red) and PAA5 nanoparticles, achieved by crosslinking PAA5/F127 0.75/1 complexes in the solution and removing F127 by dialysis at pH 7 (black).
Fig. S10. TEM images of PAA₅ nanoparticles with (a) low and (b) high density of crosslinks (CR) prepared from solutions at pH 2 (left) and pH 7 (right). The histograms of the particle diameters were calculated by analyzing ~ 50 particles in the TEM images.