

## Supplementary Materials

### **pH- and Thermo-Responsive Water-Soluble Smart Polyion Complex (PIC) Vesicle with Polyampholyte Shells**

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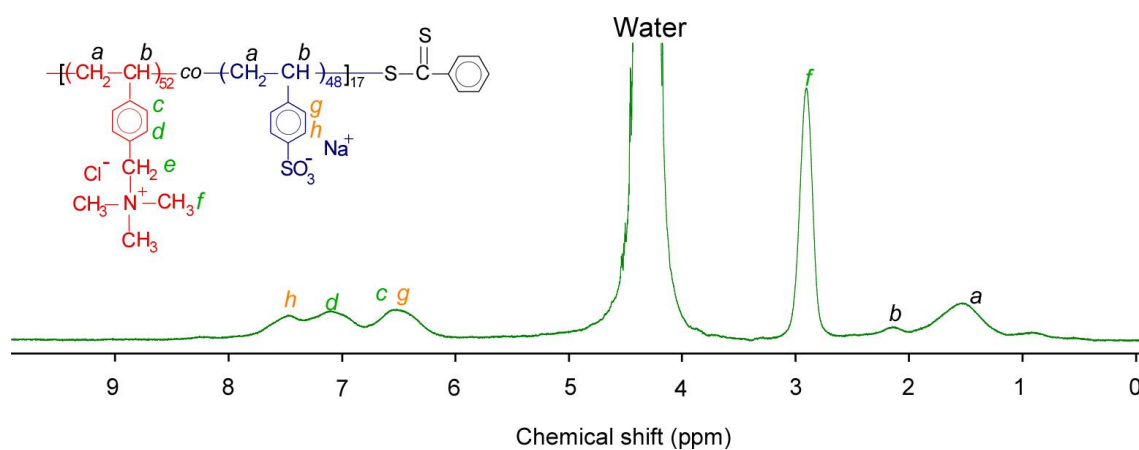
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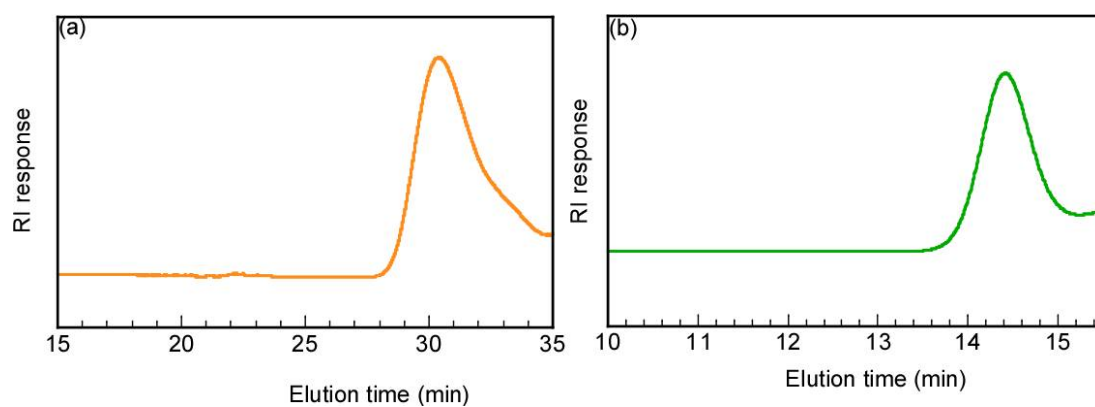
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Shin-ichi Yusa

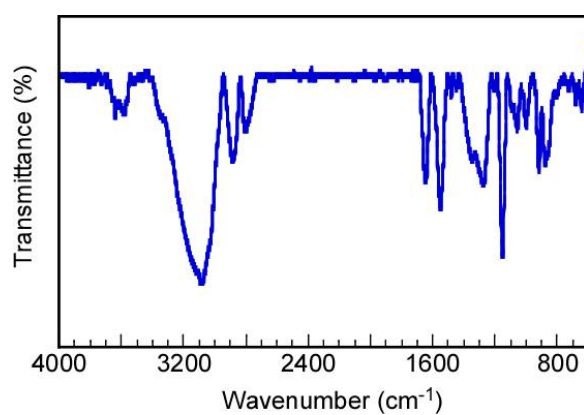
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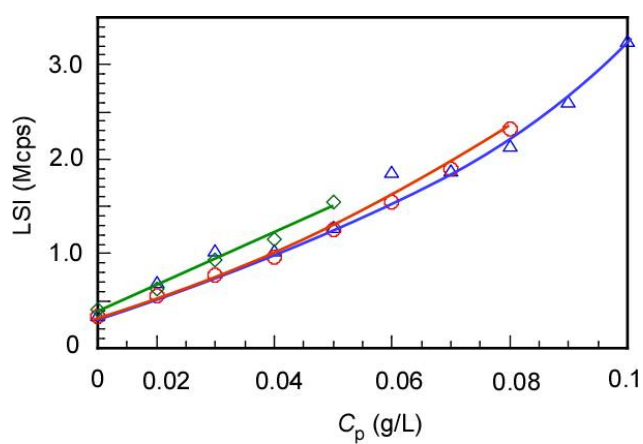
**Figure S1.**  $^1\text{H}$  NMR spectrum for  $P(VBTAC/NaSS)_{17}$  in  $\text{D}_2\text{O}$  containing 1.2-M NaCl at 70 °C.



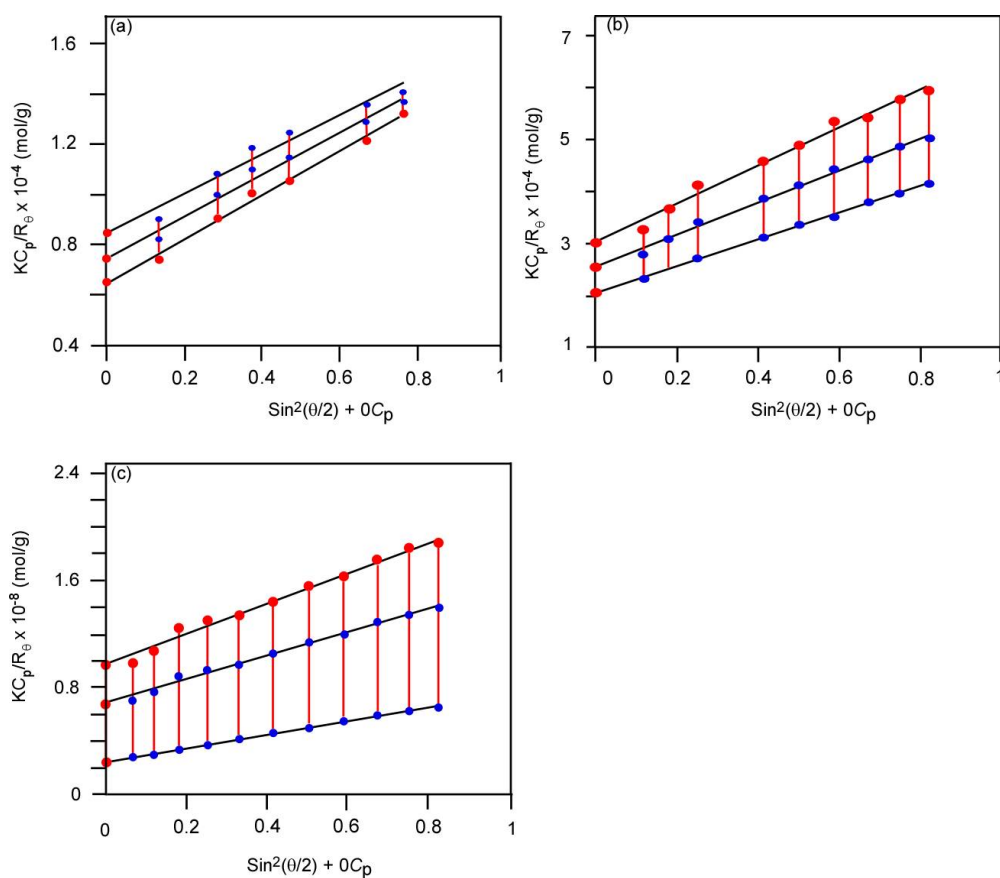
**Figure S2.** Gel-permeation chromatography (GPC) elution curves for (a)  $P(VS)_{17}A_{50}$  and (b)  $PAAc_{49}$  monitored with refractive index (RI) detector working at 40 °C.



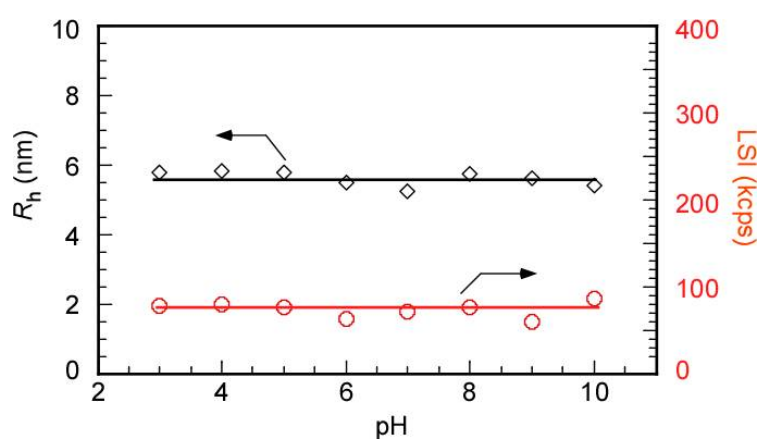
**Figure S3.** FTIR spectrum for P(VS)<sub>17</sub>A<sub>50</sub>.



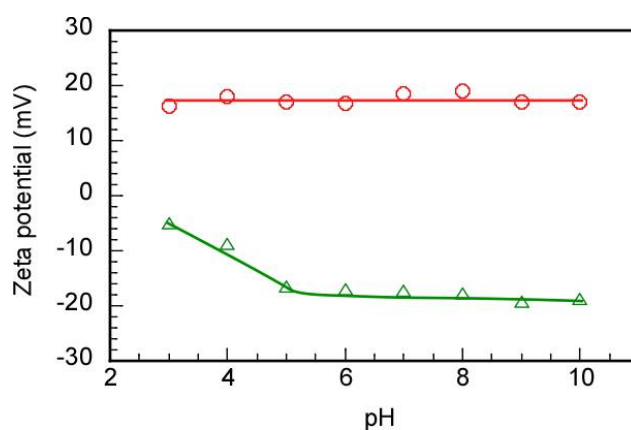
**Figure S4.** Light scattering intensity (LSI) for the P(VS)<sub>17</sub>A<sub>50</sub>/PAAc<sub>49</sub> PIC vesicles with  $f^+ = 0.5$  in water at pH 10 as a function of polymer concentration after mixing P(VS)<sub>17</sub>A<sub>50</sub> and PAAc<sub>49</sub>. At 25 °C the PIC aggregates solution at 0.1 (triangle), 0.08 (circle), and 0.05 (diamond) g/L were diluted with pH 10 aqueous solution.



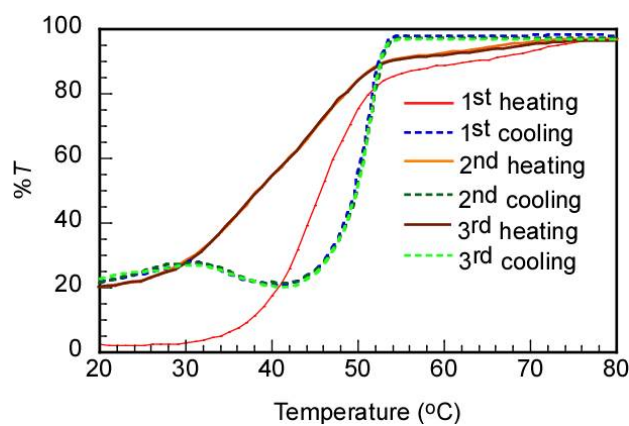
**Figure S5.** Typical examples of Zimm plots for (a) P(VS)<sub>17</sub>, (b) PAAc<sub>49</sub>, and (c) the P(VS)<sub>17</sub>A<sub>50</sub>/PAAc<sub>49</sub> PIC vesicle with  $f^+ = 0.5$  in aqueous solutions at pH 10.



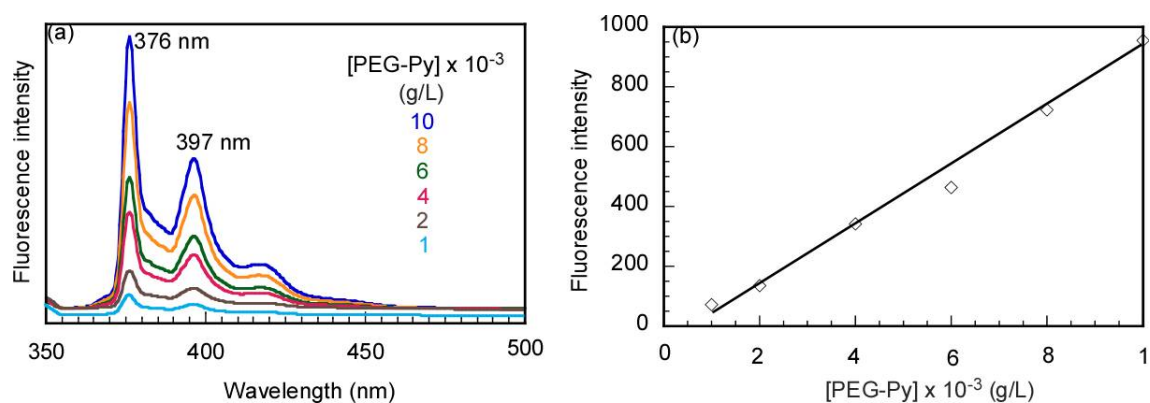
**Figure S6.** Hydrodynamic radius ( $R_h$ , diamond) and light scattering intensity (LSI, circle) for P(VS)<sub>17</sub>A<sub>50</sub> at  $C_p = 2.0 \text{ g/L}$  in water as a function of pH at 25 °C.



**Figure S7.** Zeta-potential for P(VS)<sub>17</sub>A<sub>50</sub> (circle) and PAAc<sub>49</sub> (triangle) in water at  $C_p = 2.0$  g/L as a function of pH at 25 °C.



**Figure S8.** Percent transmittance (% $T$ ) at 700 nm for the 0.1-M NaCl aqueous P(VS)<sub>17</sub> solution at  $C_p = 1.0$  g/L as a function of temperature upon the heating and cooling processes.



**Figure S9.** (a) Fluorescence spectra for PEG-Py in water at pH 10 excited at 334 nm at various PEG-Py concentrations ([PEG-Py]) and (b) a calibration curve of fluorescence intensity at 376 nm using [PEG-Py] in water at pH 10.