Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Pyridine-functional diblock copolymer nanoparticles synthesized via RAFT-mediated polymerization-induced self-assembly: effect of solution pH

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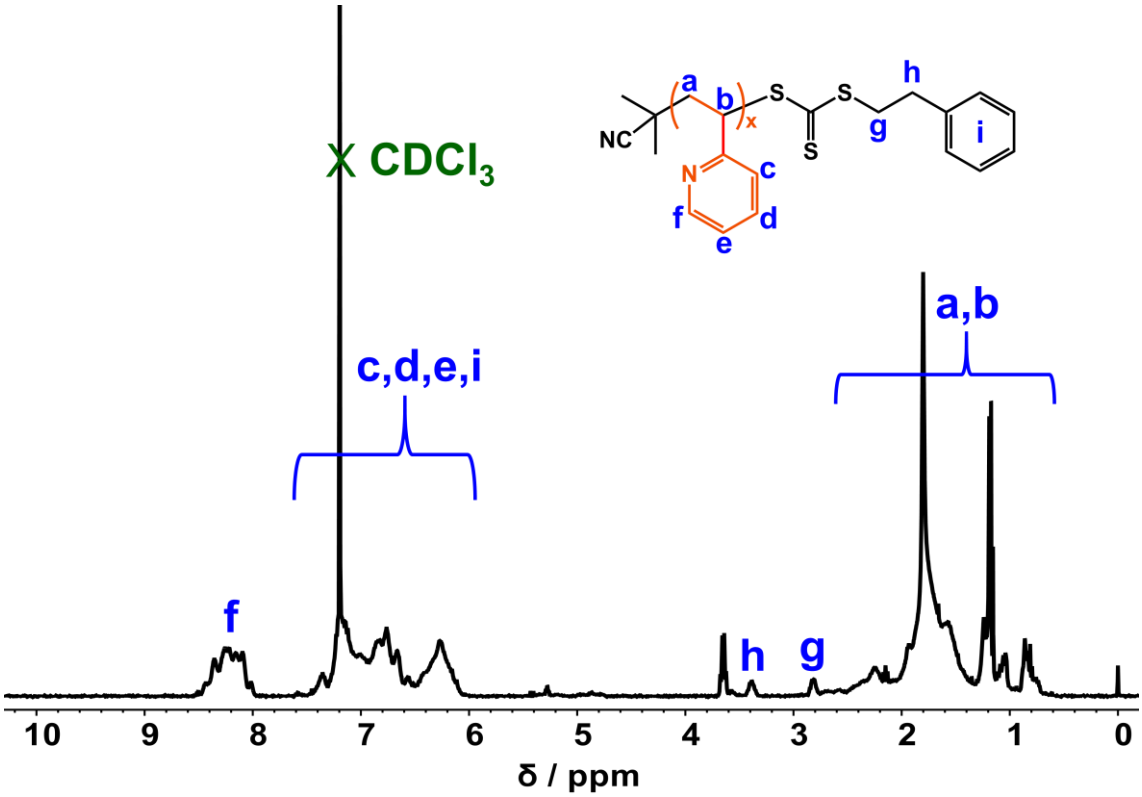

Figure S1. ^{1}H NMR spectrum of $P2VP_{32}$ macro-CTA. The sample was dissolved in $CDCl_3$ prior to NMR analysis. The degree of polymerization (DP) for this macro-CTA was calculated by comparing the integrated proton signals corresponding to pyridine at 8.1–8.6 ppm (f) with that corresponding to the two protons on methylene group of the PETTCCP at 3.4–3.5 ppm (h).

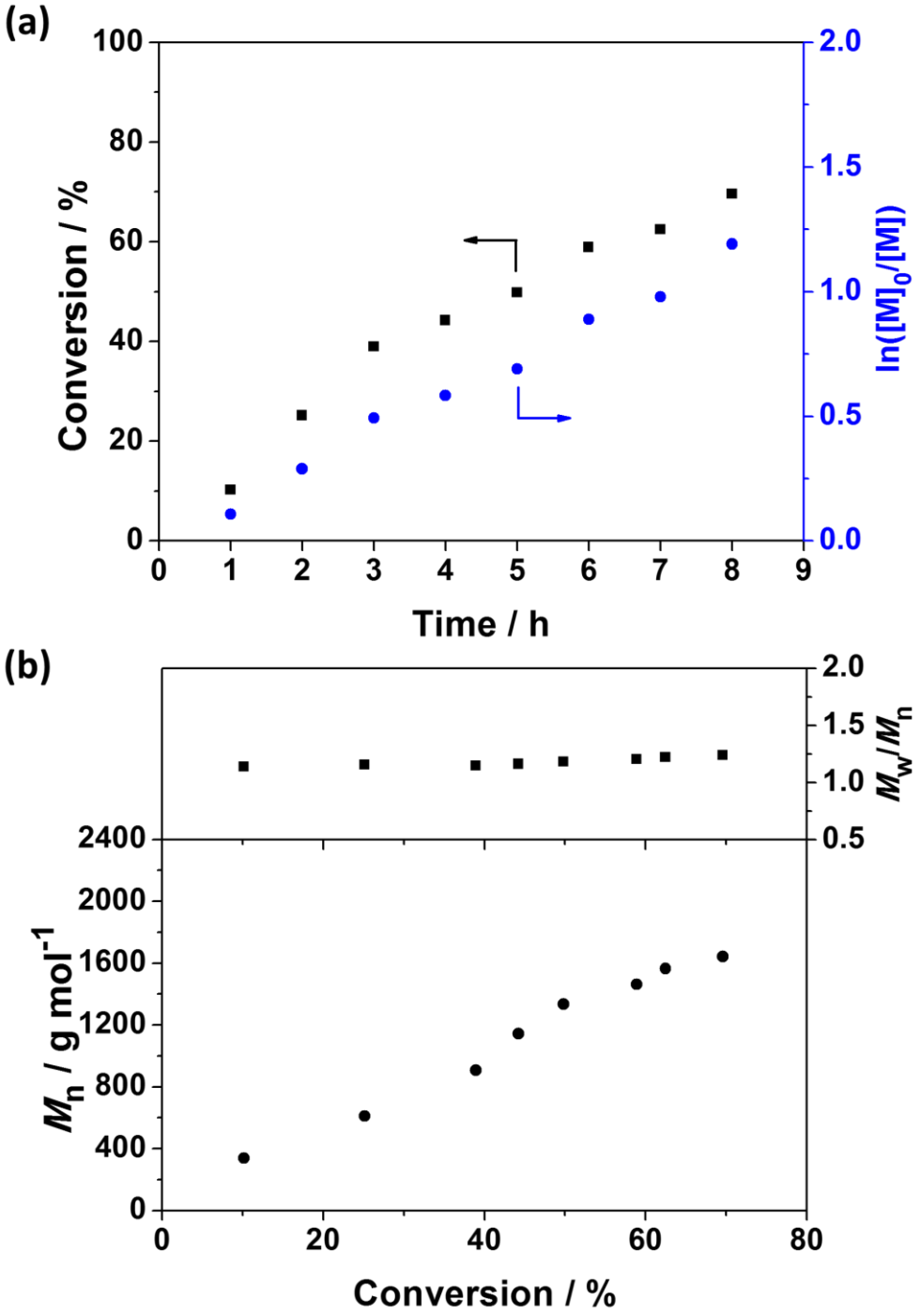

Figure S2. Kinetic studies for RAFT solution polymerization of 2VP (target DP 50) using PETTCCP as a CTA in ethanol at 70 °C (15% w/w): (a) conversion and semi-logarithmic kinetics versus reaction time and (b) M_w/M_n and M_n versus monomer conversion.

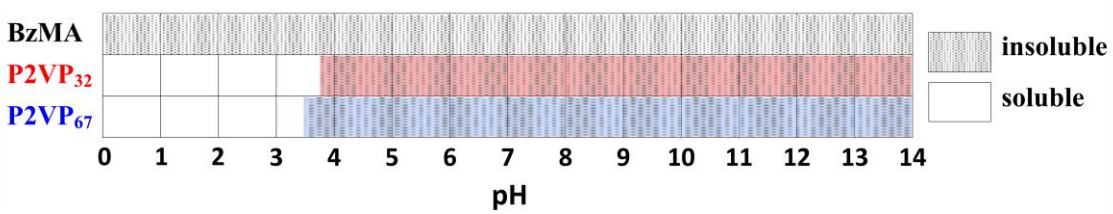

Figure S3. Solubility of BzMA, $P2VP_{32}$, and $P2VP_{67}$ in water at different pH. Solubility tests were conducted at 24 °C and at concentrations of 0.3 g mL^{-1} and 5 mg mL^{-1} for BzMA and $P2VP_x$, respectively.

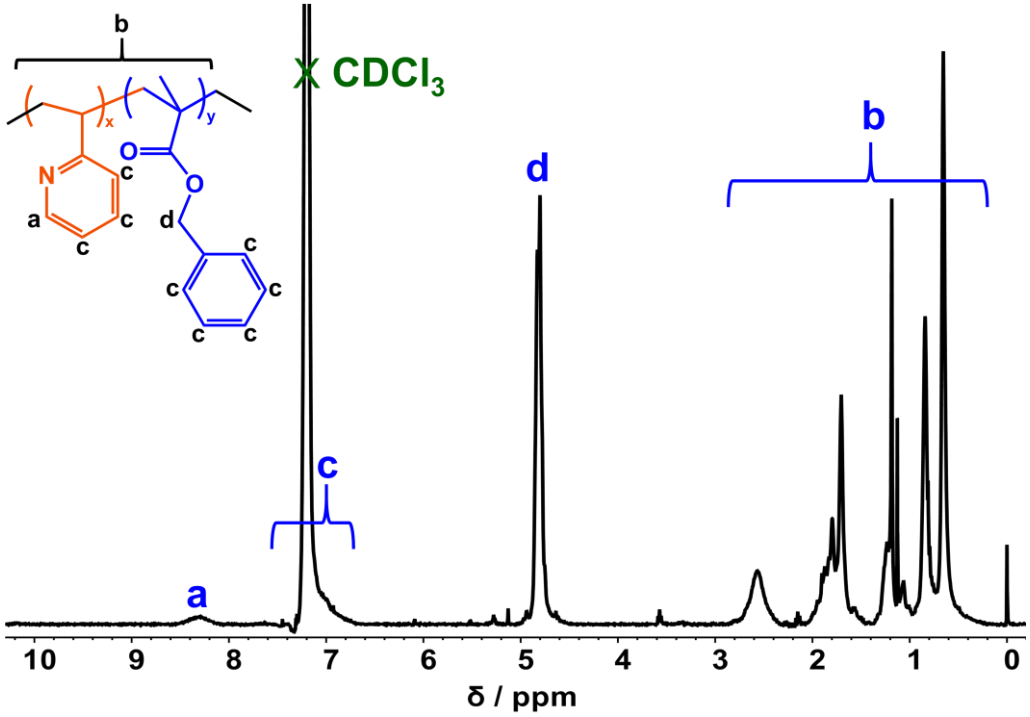

Figure S4. Representative ^1H NMR spectra of $P2VP_{32}$–$PBzMA_{50}$. The sample was dissolved in $CDCl_3$ prior to NMR analysis. The 2VP and BzMA contents in the diblock copolymer were calculated by comparison of the integration of a proton on pyridine group of P2VP at 8.1–8.6 ppm (a) with the two protons on methylene of PBzMA at 4.5–5.0 ppm (d).

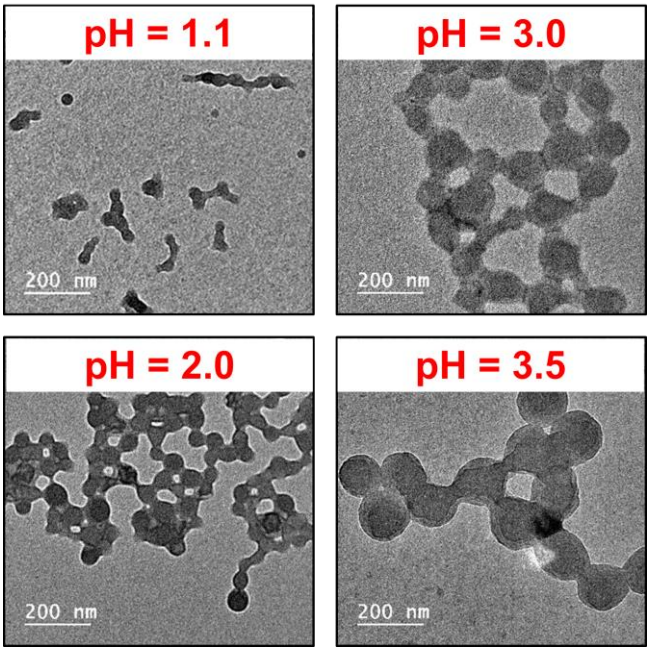

Figure S5. Representative TEM images of $P2VP_{67}$–$PBzMA_{300}$ diblock copolymer nanoparticles prepared at 10% w/w solids *via* RAFT-mediated PISA in water at 70 °C and varying solution pH ranging from 1.1 to 3.5.

Table S1. Summary of target copolymer composition, pH, mean hydrodynamic diameter, molar mass, and molar mass distribution obtained for $P2VP_x$–$PBzMA_y$ (V_x–B_y) diblock copolymers synthesized at 10% w/w via RAFT-mediated PISA in water at 70 °C.

Entry	Target composition[a]	Solution pH	D_h[b] / nm	M_n[c] / g mol^{-1}	M_w[c] / g mol^{-1}	M_w/M_n[c]
1	V_{32}–B_{300}	1.0	74 (0.063)	40.4	55.6	1.38
2	V_{32}–B_{300}	1.5	90 (0.024)	47.8	77.1	1.61
3	V_{32}–B_{300}	2.0	113 (0.070)	47.0	79.0	1.68
4	V_{32}–B_{300}	2.5	142 (0.040)	46.0	81.6	1.77
5	V_{32}–B_{300}	3.0	162 (0.051)	48.3	102.1	2.12
6	V_{32}–B_{300}	3.5	193 (0.070)	51.6	121.2	2.35
7	V_{67}–B_{300}	1.1	59 (0.040)	18.7	25.0	1.34
8	V_{67}–B_{300}	1.5	62 (0.053)	28.4	39.1	1.38
9	V_{67}–B_{300}	2.0	74 (0.043)	29.1	43.7	1.50
10	V_{67}–B_{300}	2.3	99 (0.046)	44.5	76.6	1.72
11	V_{67}–B_{300}	3.0	147 (0.016)	57.2	98.7	1.73
12	V_{67}–B_{300}	3.5	166 (0.018)			
13	V_{32}–B_{50}	2.0	52 (0.092)			
14	V_{32}–B_{100}	2.0	63 (0.049)			
15	V_{32}–B_{500}	2.0	196 (0.036)	75.7	167.3	2.21
16	V_{32}–B_{700}	2.0	241 (0.041)			
17	V_{32}–B_{900}	2.0	317 (0.076)	124.8	323.0	2.59

[a] All monomer conversions determined *via* gravimetry were higher than 99% after polymerization at 70 °C for 24 h. [b] Obtained *via* DLS analysis, where DLS polydispersity index values are indicated in brackets. Samples were diluted in water at pH 2 to minimize potential coagulation. [c] Determined *via* THF GPC analysis. Samples were diluted in deionized water, and then titrated to above pH 7 to decrease the protonation of P2VP stabilizer and increase the solubility of P2VP–PBzMA diblock copolymers in THF. The M_n and M_w/M_n values determined using the P2VP–PBzMA copolymer peaks at a retention time of 18-27 min.