Supporting Information for:

Synthesis and Rheological Characterization of Poly(vinyl acetate-*b*-vinyl alcohol-*b*-vinyl acetate) Triblock Copolymer Hydrogels

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Table S1. Molecular characteristics of P(VClAc-*ran*-VAC)/PVAc block copolymers

Initial Block				Chain Extension			Block Copolymer			
CTA	F_{VAc}[a]	M_n (kg/mol)[b]	$Đ$[b]	[CTA] (mM)	[CTA]:[I]	t_{rxn} (h)	F_{VAc}[a]	$N_{n,endblock}$[e]	M_n (kg/mol)[b]	$Đ$[b]
1	0.45	5.8	1.26	15	10:1[c]	4.5	0.80	97	12.6	1.48
2	0.45	14.3	1.23	10	8:1[d]	1.5	0.78	200	27.9	1.40
2	0.25	13.1	1.32	12	8:1[d]	0.75	0.74	241	32.9	1.42
2	0.22	18.6	1.39	12	8:1[d]	0.75	0.68	254	40.1	1.52
2	0.24	23.4	1.38	12	15:1[d]	1.5	0.64	225	42.7	1.60

[a]Mole fraction of VAc in polymer determined by quantitative ^{1}H NMR in $CDCl_3$. [b]Determined by SEC in THF at 40 °C using a Mark-Houwink corrected calibration curve for PVAc (see Experimental section). [c] I = 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40)) with T_{rxn} = 80 °C and [VAc] = 3.3 M in $ClCH_2CH_2Cl$. [d] I = 1,1'-azobisisobutyronitrile (AIBN) with reaction temperature T_{rxn} = 60 °C in bulk [VAc] = 10.8 M. [e] $N_{n,endblock}$ = end block number average degree of polymerization from chain extension determined from quantitative ^{1}H NMR analysis based on the initial block molecular weight from SEC.

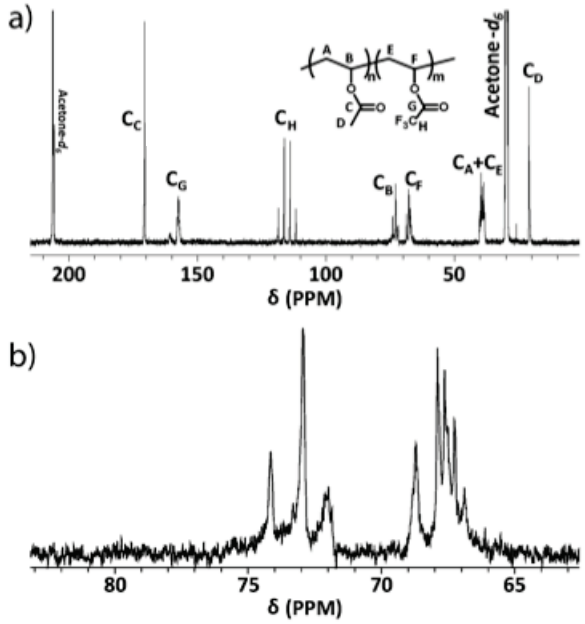

Figure S1. (a) ^{13}C NMR spectra of $VOH_{56}Ac_{97}$ after treatment with trifluroacetic anhydride (P(VTFA-*b*-VAc)), and (**b**) an enlargement of the methine carbon region, demonstrating selective hydrolysis of P(VAc-*r*-VClAc)-*b*-VAc) to produce P(VOH-*b*-VAc).

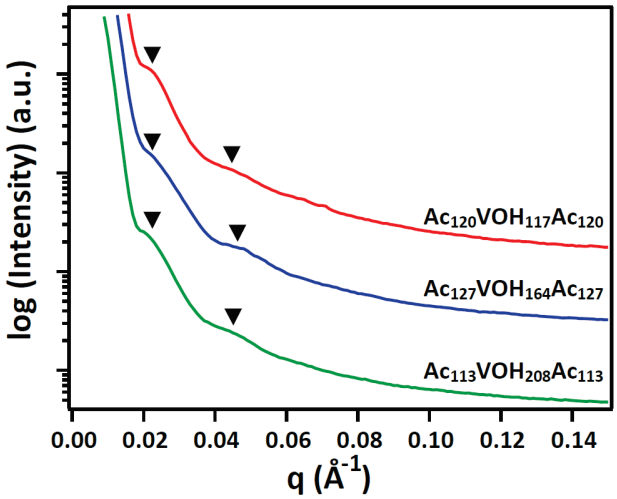

Figure S2. Azimuthally-integrated synchrotron SAXS intensity profiles of hydrogel samples. The black triangles indicate the position of form factor scattering maxima for each sample, which confirms that these P(VAc-*b*-VOH-*b*-VAc) hydrogels are microphase separated.

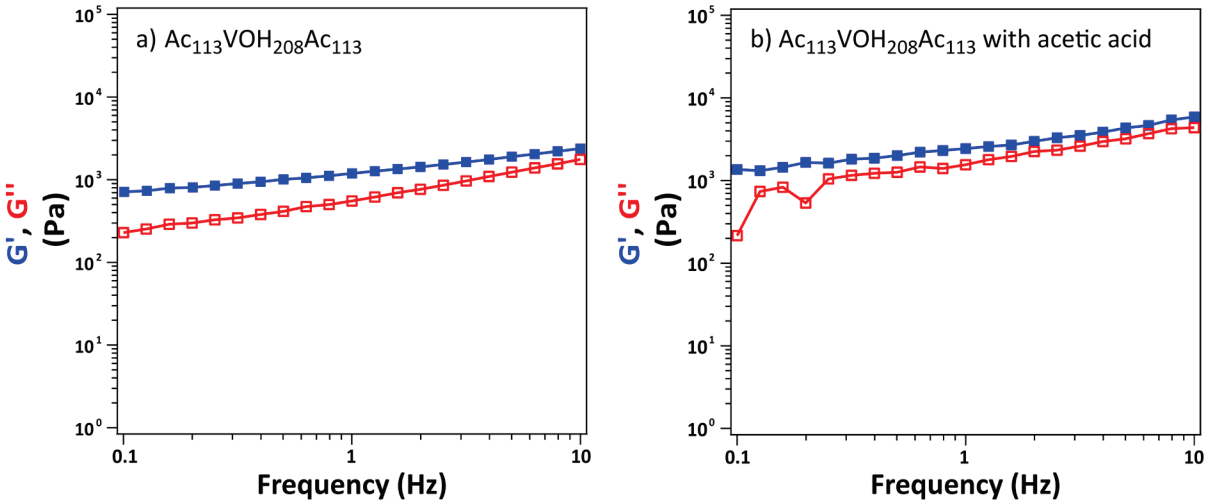

Figure S3. Isothermal frequency sweep for $Ac_{113}VOH_{208}Ac_{113}$ at $|\gamma| = 1\%$ strain at 25 °C swollen in (**a**) Milli-Q water and (**b**) in 1% (*v*/*v*) $CH_3COOH(aq)$ for 4 h at 22 °C. The weakly frequency dependent storage and loss moduli of both the native gel ($G' \sim \omega^{0.26}$, $G'' \sim \omega^{0.44}$) and the CH_3COOH (*aq*) treated sample ($G' \sim \omega^{0.32}$, $G'' \sim \omega^{0.48}$) are comparable to those previously reported for triblock copolymer hydrogels (see main article for details).

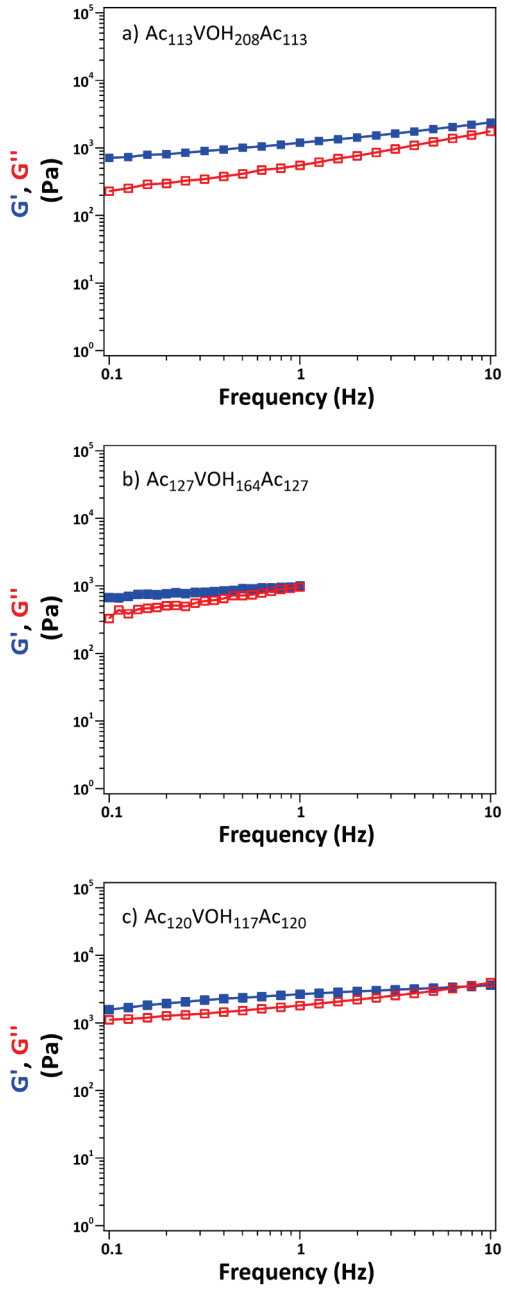

Figure S4. Isothermal frequency sweeps for (**a**) $Ac_{113}VOH_{208}Ac_{113,}$ (**b**) $Ac_{127}VOH_{164}Ac_{127}$ and (**c**) $Ac_{120}VOH_{117}Ac_{120}$ at $|\gamma|$ = 1% strain at 25 °C illustrate that the chain length of the PVOH segment has little effect on the frequency-dependent rheological behavior of these hydrogels.

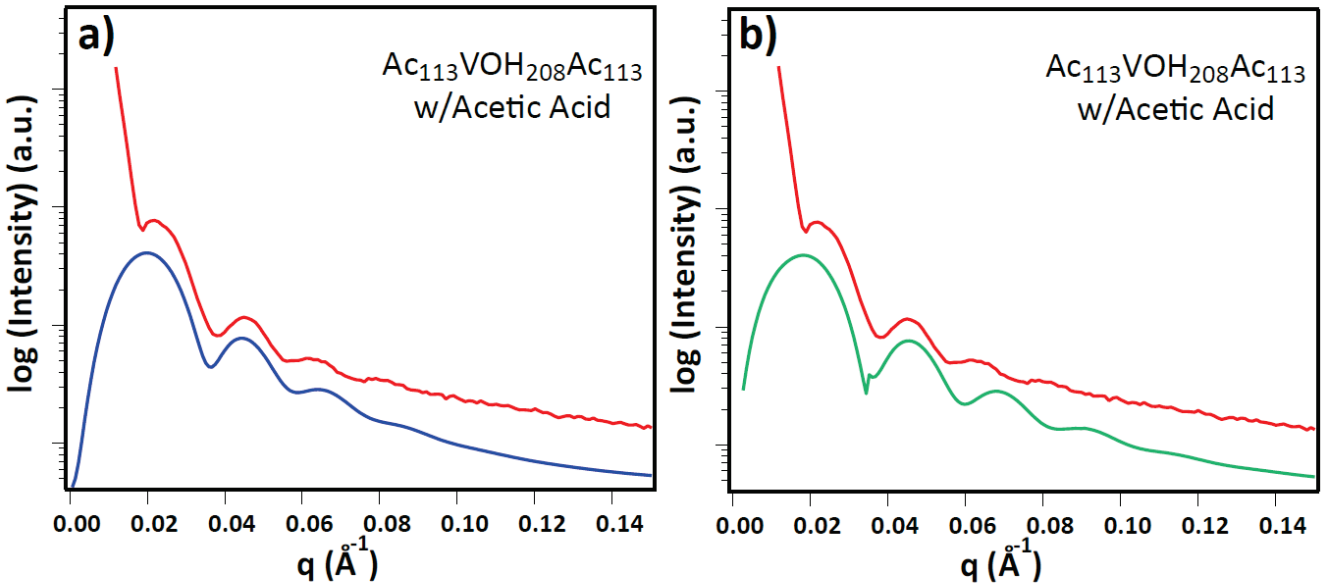

Figure S5. (**a**) Overlay of synchrotron SAXS pattern for $Ac_{113}VOH_{208}Ac_{113}$ soaked with 10% (*v/v*) $CH_3COOH(aq)$ with a best form factor fit for spherical micelles with a diameter $d = 16.5 \pm 2.1$ nm. (**b**) Overlay of the same synchrotron SAXS pattern for $Ac_{113}VOH_{208}Ac_{113}$ soaked with 10% (*v/v*) $CH_3COOH(aq)$ with a poor form factor fit for cylindrical micelles with a diameter $d = 14.8 \pm 1.9$ nm, indicating that the hydrogel is more likely comprised of spherical micelles in a $PVOH/H_2O$ matrix phase.