Electronic Supplementary Information

Rapidly Responding pH and Temperature-Responsive Poly (*N*-Isopropylacrylamide)-Based Microgels and Assemblies

Andrews Ahiabu[†] *and Michael J. Serpe**[†]

[†]*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2*

*email: michael.serpe@ualberta.ca

Scheme S1. Synthesis of Butylacrylic acid (BAAc)

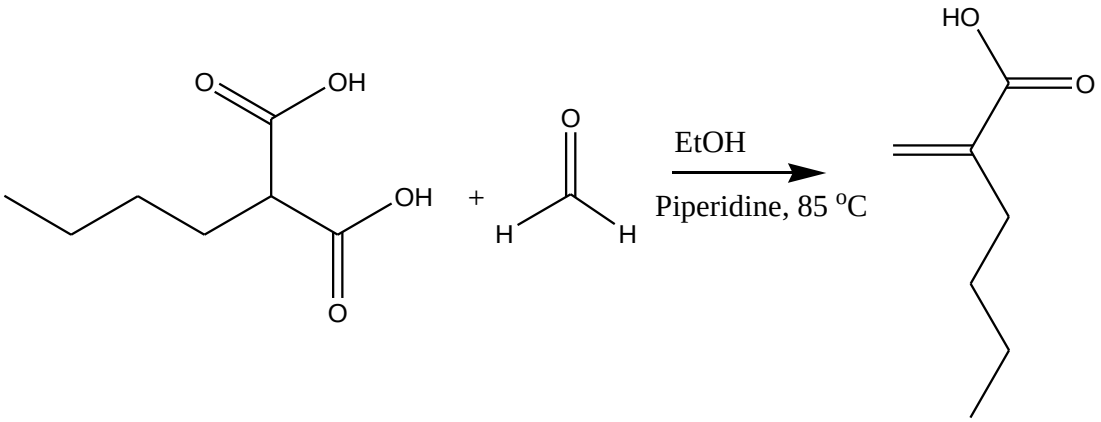

Table S1. Distinctive IR functional groups and their representative vibrational frequencies for both BAAc monomer and pNIPAm-co-BAAc microgels

Functional group	Wavenumbers (cm^{-1})
N-H stretching	3305
CH_3 stretching	2971
O-H stretching	2960
=C-H stretching	2875
-C=O (carboxyl stretching)	1697
Amide I –C=O stretching	1649
C=C stretching	1629
Amide II – NH bending	1530
C-H bending	1459
C-H bending (from BAAc)	1442
Isopropyl stretching	1387
C-O stretching (from BAAc)	1225
C-O stretching	1173
=C-H bending	951

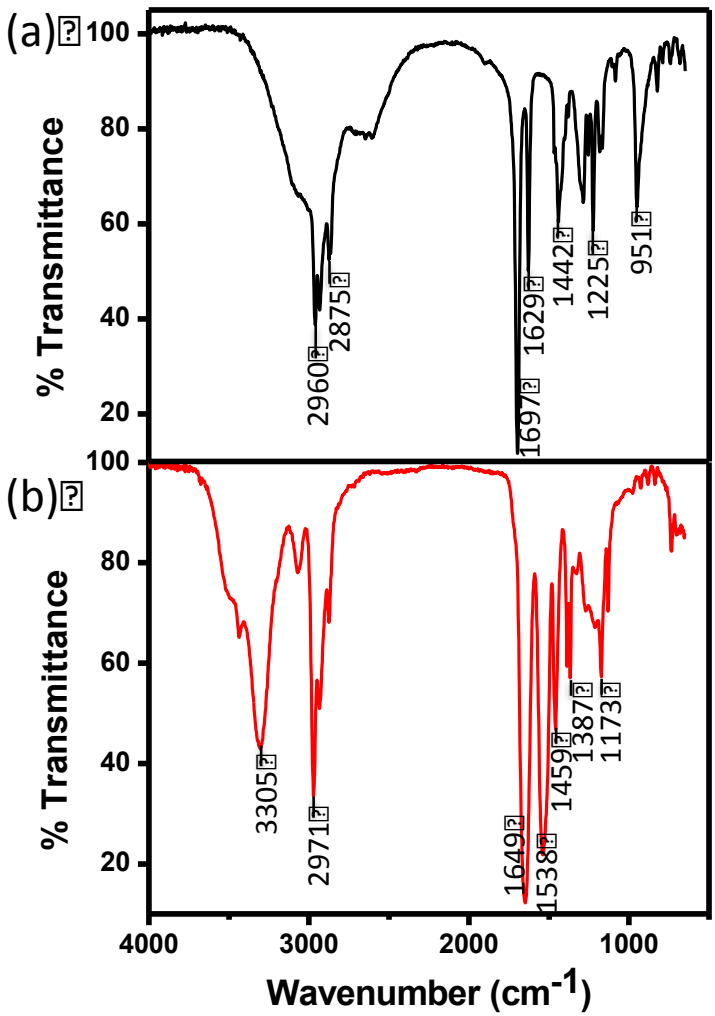

Figure S1. FTIR spectra of (a) BAAc and (b) pNIPAm-co-BAAc

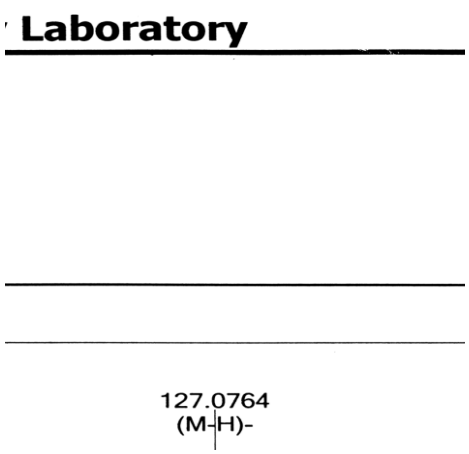

Figure S2: Mass spectrum of BuAAc, with the molecular ion peak of (M-H) at 127.0764.

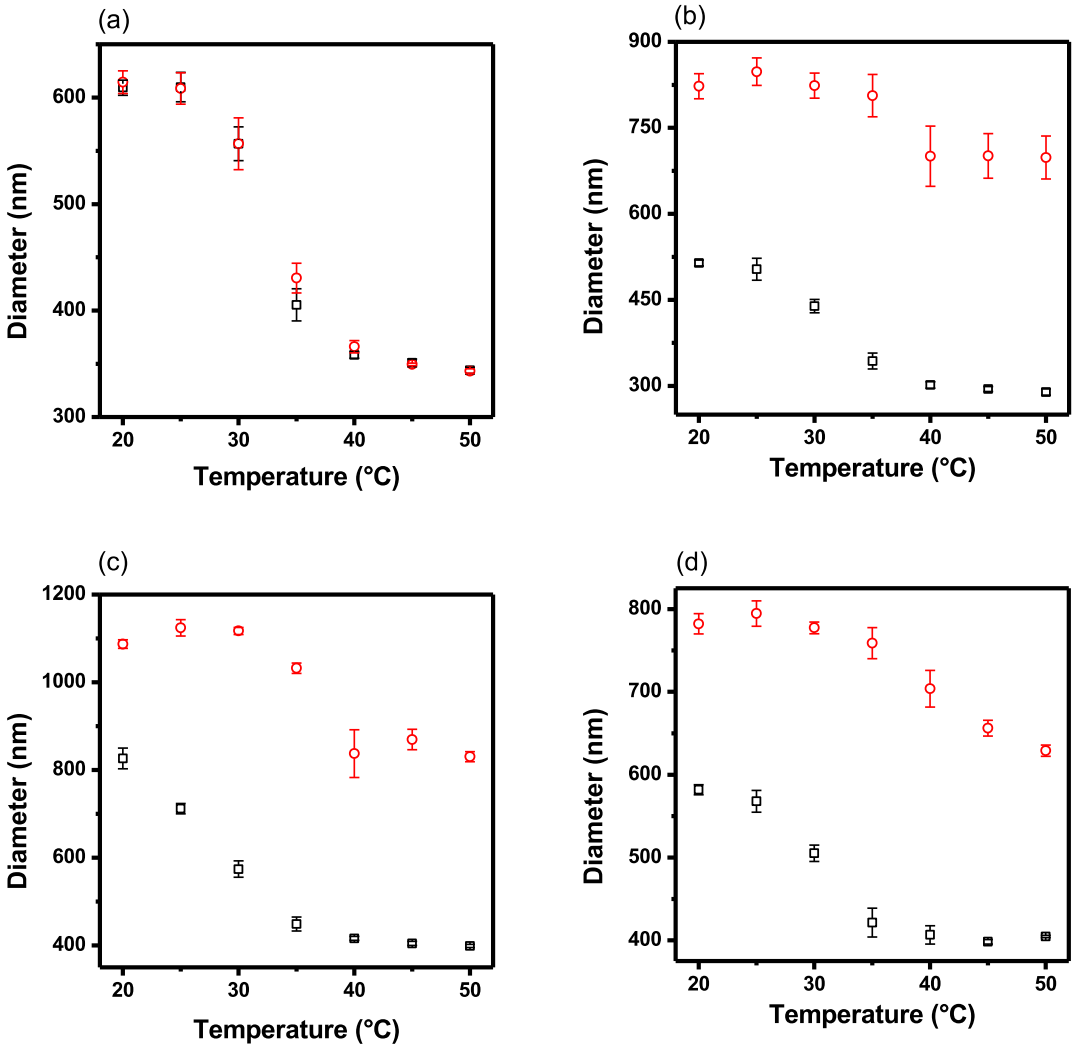

Figure S3. Microgel diameter as a function of solution temperature at the indicated solution pHs. (a) pNIPAm, (b) pNIPAm-co-MAAc, (c) pNIPAm-co-EAAc, and (d) pNIPAm-co-BAAc at (□) pH 3 and (○) pH 10.

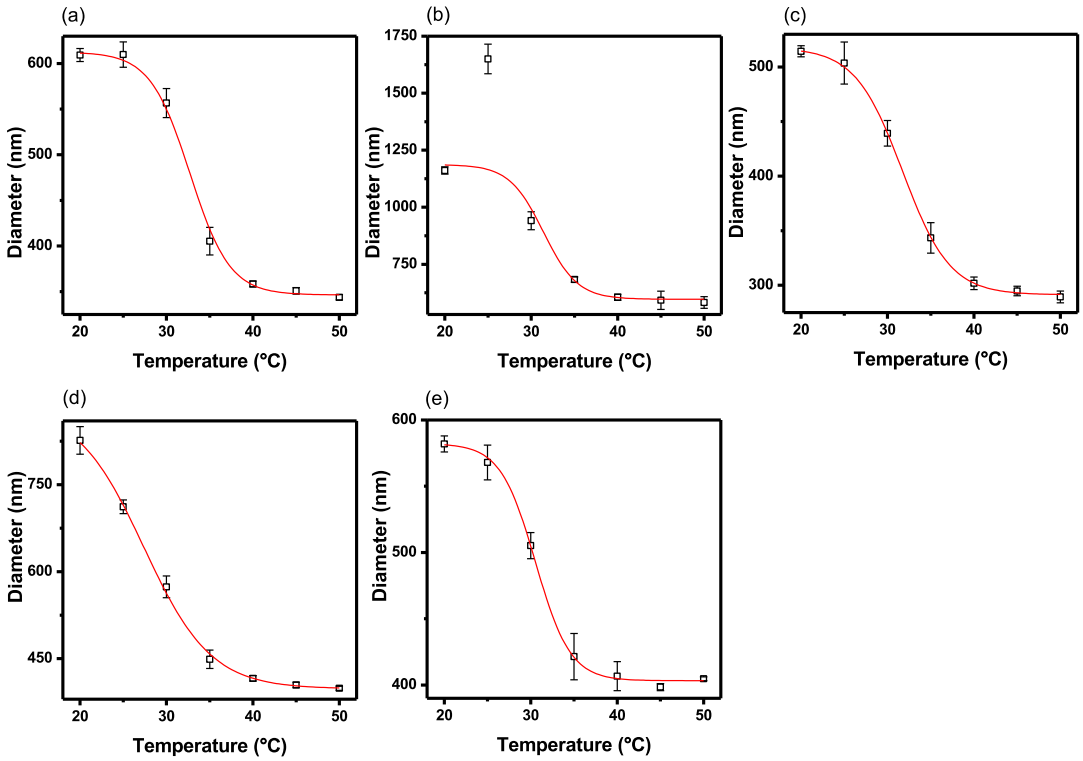

Figure S4. Microgel diameter as a function of temperature for (a) pNIPAm, (b) pNIPAm-co-AAc, (c) pNIPAm-co-MAAc, (d) pNIPAm-co-EAAc, and (e) pNIPAm-co-BAAc microgels. Data points represent average of three measurements with error bars representing the standard deviation. Data were fit to a Boltzmann sigmoidal curve fitting function using OriginLab program software and the LCST determined.

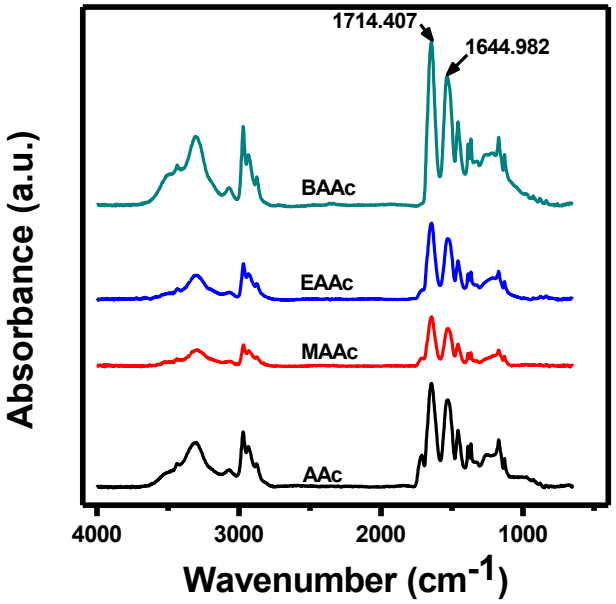

Figure S5. FTIR spectra of pNIPAm-co-BAAc, pNIPAm-co-EAAc, pNIPAm-co-MAAc, and pNIPAm-co-AAc. The ratio of absorbance at 1714.407 cm^{-1} (carboxylic acid -C=O) to the absorbance at 1644.982 cm^{-1} (amide I -C=O) was used to estimate the amount of comonomer present in the microgels.

Table S2. Comonomer feed and composition in microgel.

Comonomer	Amount added (g)	Amount in microgel (g)[1]	-C=O[2a]	-C=O[2b]	Ratio[2c]
Acrylic acid (AAc)	0.1011	0.0922	0.083	0.274	0.303
Methacrylic acid (MAAc)	0.1207	0.0810	0.021	0.13	0.162
Ethylacrylic acid (EAAc)	0.1405	0.0869	0.022	0.2	0.110
Butylacrylic acid (BAAc)	0.1798	0.0229	0.003	0.43	0.007

[1]Amount estimated from potentiometric and conductometric titration. [2a]Absorbance at 1714.407 cm^{-1} (carboxylic acid -C=O), [2b] absorbance at 1644.982 cm^{-1} (amide I -C=O), [2c] ratio of absorbance at 1714.407 cm^{-1} to 1644.982 cm^{-1}.

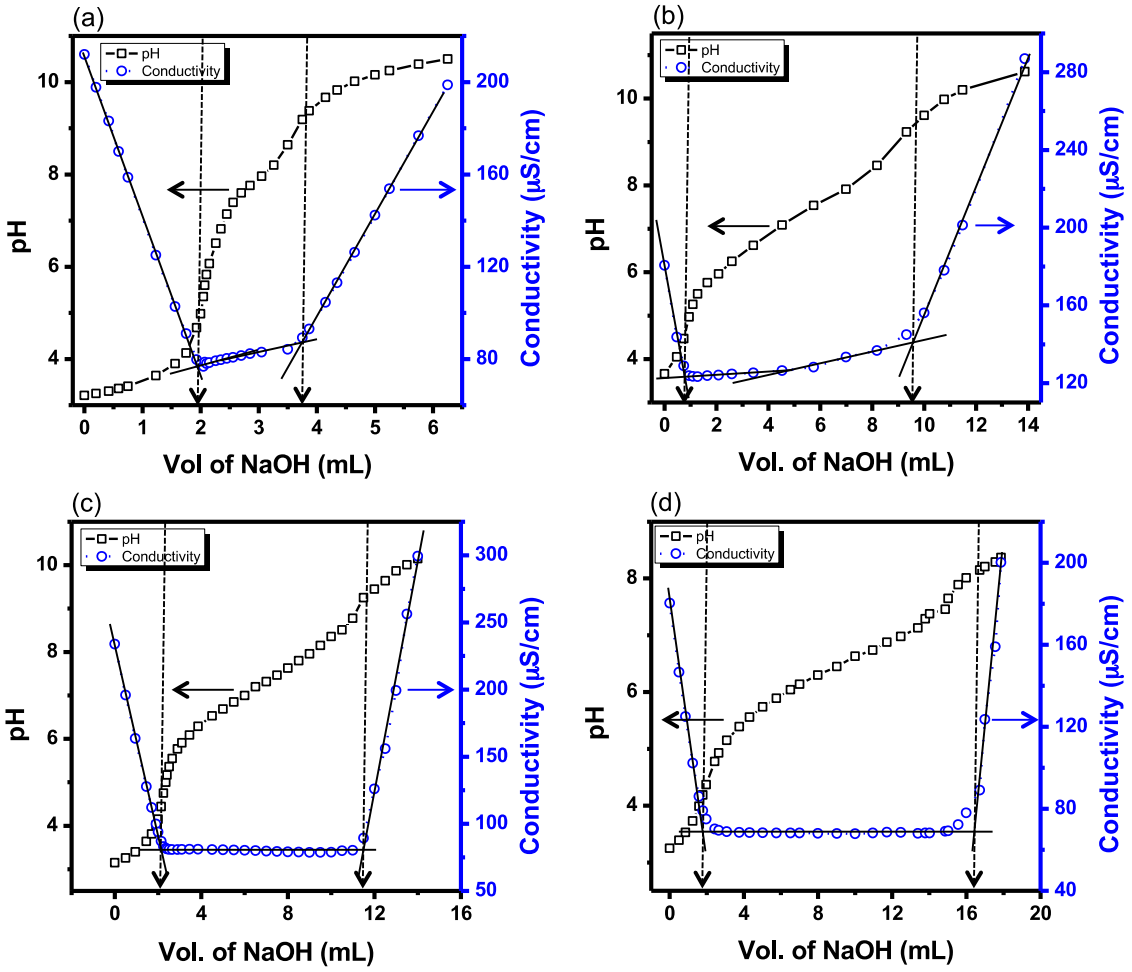

Figure S6. Potentiometric and conductometric titration of (a) pNIPAm-co-BAAc, (b) pNIPAm-co-EAAc, (c) pNIPAm-co-MAAc, and (d) pNIPAm-co-AAc. Initial pH of each microgel solution was reduced to about 3 by addition of 1.0 M HCl and titrated with 0.0101 M NaOH. The first minima on the conductivity measurement curves (first arrow) corresponds to the volume of NaOH required to neutralize any excess strong acid, while the second minima indicate where all the acid groups in the microgels were neutralized.