Supporting Information File for:

Aminated Thermoresponsive Microgels Prepared from the Hofmann Rearrangement of Amides Without Side Reactions

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Figure SI 1 show the proton NMR spectrum for AMI-0. The methacrylamide (MAM) content, estimated from the peak areas for isopropyl proton at 4 ppm relative to the methyl protons and the backbone protons, was 6.7 wt% (0.79 mmol/g), which was considerably lower than the 16 wt% feed. The reactivity ratios for MAM and NIPMAM are not published, however, we expected them to be close to 1 in analogy to acrylamide and NIPAM.[1]

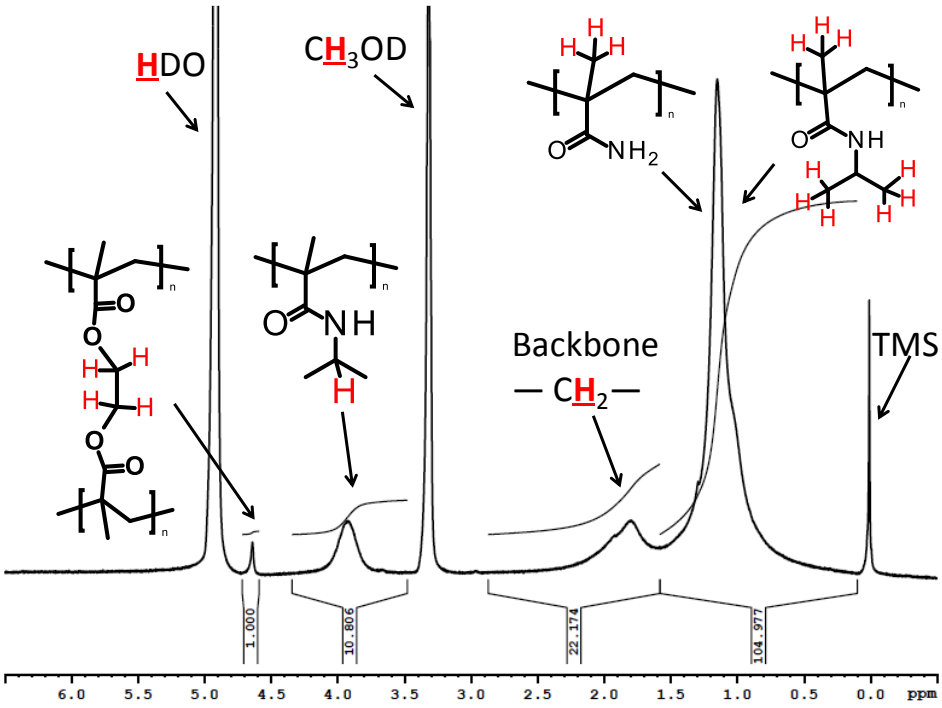

Figure SI 1. ^{1}H-NMR Spectrum of AMI-0 Microgel.

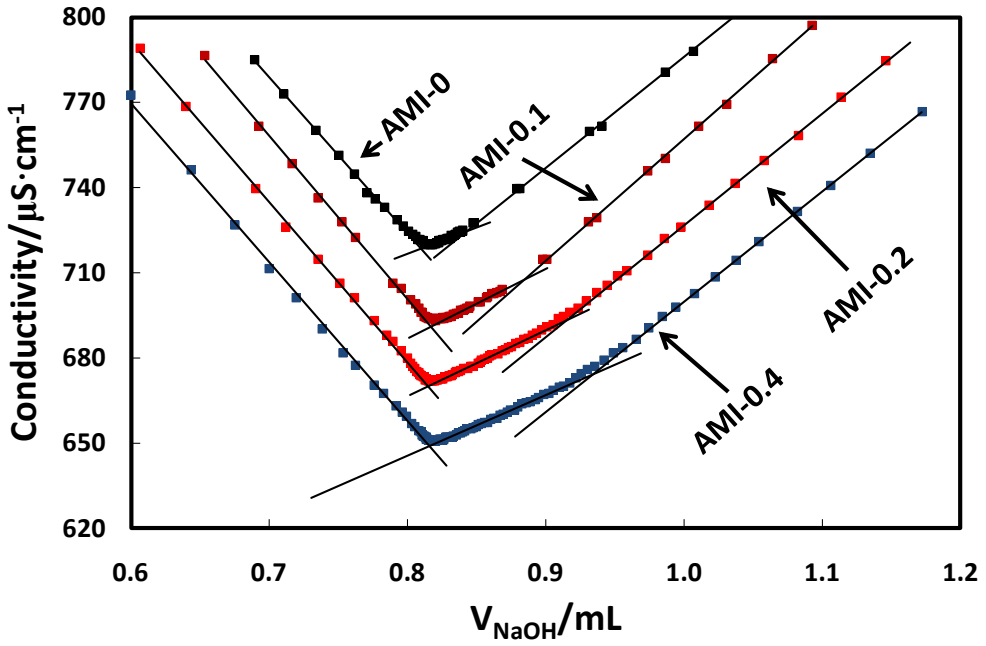

Figure SI 2. Conductometric titration curves for the AMI series of microgels after Hofmann rearrangement reactions.

The following results show that CON-0, containing only NIPMAM and MAM residues, was not modified in the presence of NaClO at high pH.

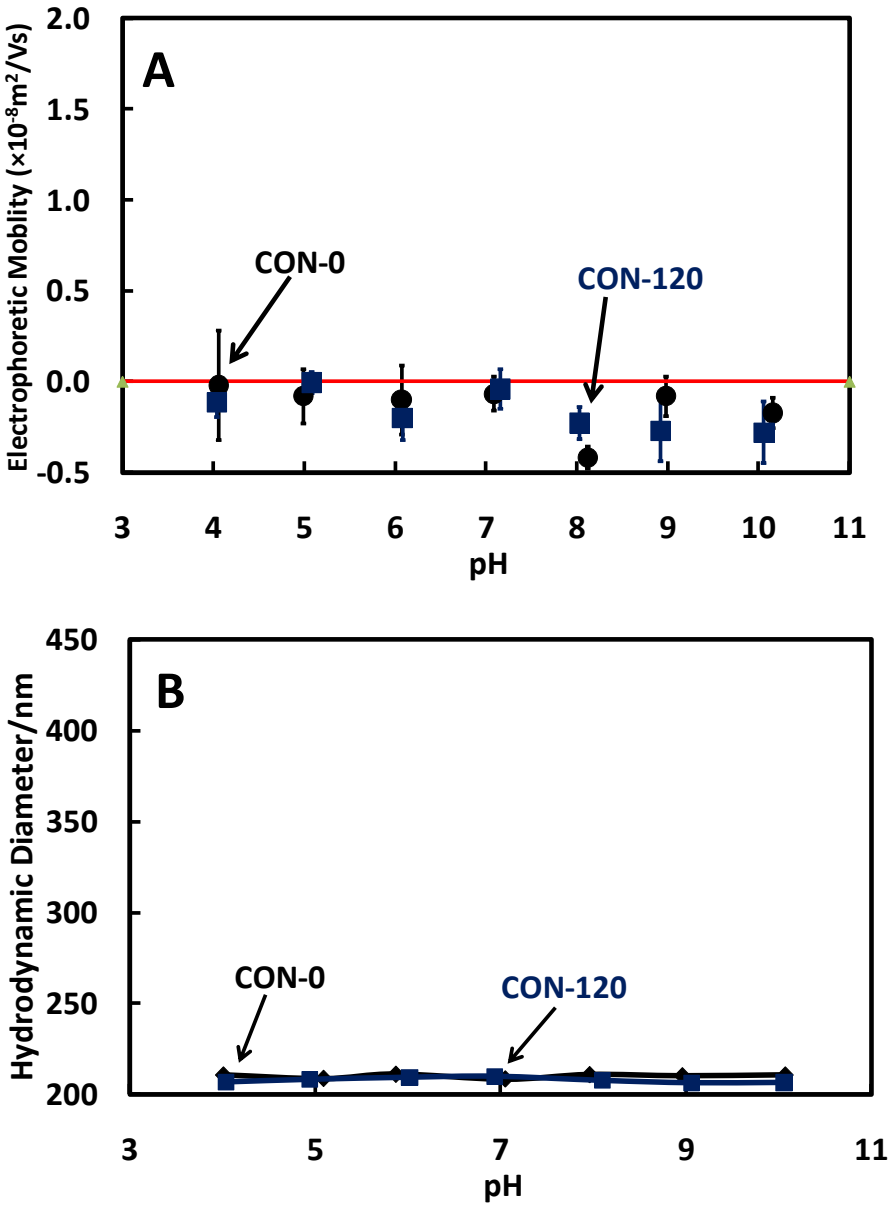

Figure SI 3. pH effect on (A) mobility and (B) diameter of CON microgels before (CON-0) and after (CON-120) Hofmann rearrangement. The measurements were conducted in 1 mM NaCl.

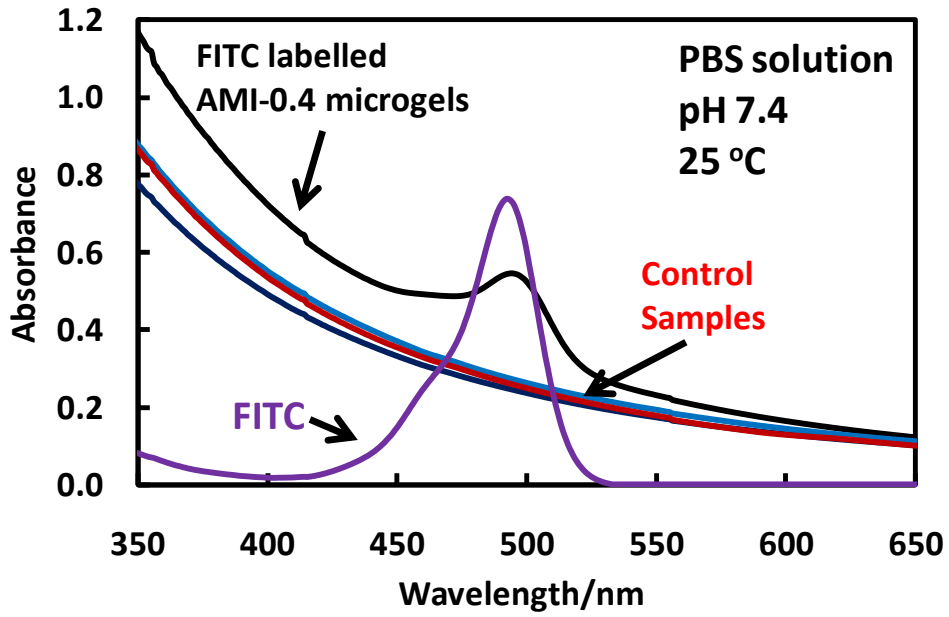

Figure SI 4. Absorbance of FITC-labelled AMI-0.4 microgels. The control samples include unlabelled AMI-0.4 microgels and AMI-0 microgels before and after react with FITC.

These results show that AMI-0.4 microgels could be conjugated with FITC where AMI-0 and CON-0 microgels showed no evidence of amine groups.

Effect of temperature on diameter of AMI microgels at pH 4 and pH 10 is shown in Figure SI 5. The volume phase transition temperature (VPTT) of CON microgels was determined around 43 ^{o}C (Supporting Information). However, no definable volume phase transition was observed both at pH 4 and pH 10 in the range of 25 ^{o}C to 50 ^{o}C. The decrease on diameter was highly suppressed at pH 4 along with temperature. At pH 4, microgels with higher amine content showed less thermosensitivity. The temperature-induced swelling ratio ($d_{25^{o}C}/d_{50^{o}C}$) was 1.14 for AMI-0.4 microgels. While at pH 10, most amines were de-ionized. Microgels showed similar thermosensitivity before and after Hofmann rearrangement. The swelling ratio ($d_{25^{o}C}/d_{50^{o}C}$) of AMI-0.4 microgels was 1.26 at pH10.

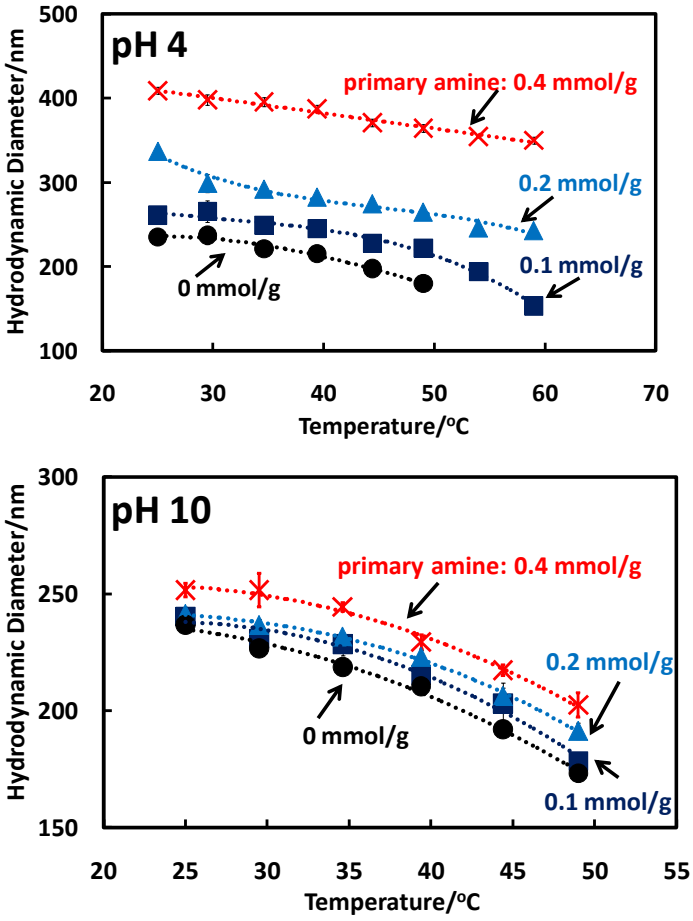

Figure SI 5. Temperature effect on diameters of AMI microgels before and after Hofmann rearrangement at pH 4 and pH 10. The measurements were conducted in 1 mM NaCl. The error bars were calculated from three repeat measurements. Dash lines are drawn as eye guidelines.

REFERENCES

1. Mumick, P. S.; McCormick, C. L., Water-soluble Copolymers. 54. N-Isopropylacrylamide-co-acrylamide Copolymers in Drag Reduction - Synthesis, Characterization, and Dilute-solution Behavior. *Polymer Engineering and Science* **1994,** 34, (18), 1419-1428.