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## **Electronic Supplementary Information**

## Single microgel degradation governed by heterogeneous nanostructures

Yuichiro Nishizawa, <sup>†a</sup> Hiroki Yokoi, <sup>†a</sup> Takayuki Uchihashi, <sup>\*c, d</sup> and Daisuke Suzuki<sup>\*a, b</sup>

<sup>a.</sup> Graduate School of Textile Science & Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567 (Japan).

<sup>b.</sup> Research Initiative for Supra-Materials, Interdisciplinary Cluster for Cutting Edge Research, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567 (Japan).

<sup>c.</sup> Department of Physics and Structural Biology Research Center, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8602 (Japan).

<sup>d.</sup> Exploratory Research Center on Life and Living Systems, National Institutes of Natural

Science, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787 (Japan).

<sup>†</sup> These authors contributed equally to this work.

\*Author to whom correspondence should be addressed.

E-mail: d\_suzuki@shinshu-u.ac.jp (D.S.)

**Results and Discussion** 



Fig. S1. Field-emission scanning electron microscopy (FE-SEM) image and the corresponding size histogram (N = 132) of the NB10 microgels.



Fig. S2. Temperature dependence of the hydrodynamic diameter  $(D_h)$  of the NB10 microgels during heating and cooling, as derived from dynamic light-scattering (DLS) measurements. The ionic strength was adjusted to 1 mM using NaCl.



**Fig. S3.** Changes to the  $D_h$  and polydispersity index (PDI) of ND microgels during degradation at different temperatures: (a) 25 °C, (b) 30 °C, (c) 35 °C, and (d) 40 °C. The microgel and NaIO<sub>4</sub> concentrations were 0.005 wt.% and 50 mM, respectively. The  $D_h$  reached its maximum value earlier and the degradation rate was increased with increasing temperature (9900 s, 8100 s, and 6000 s at 25 °C, 30 °C, and 35 °C, respectively). In contrast, at 40 °C, which was defined as the semi-swollen state, little swelling of the microgels was observed, and the decrease in  $D_h$  was significantly delayed (to 10800 s) compared to that at 35 °C.



**Fig. S4.** Time dependence of the (a) height images, (b) phase images, (c) 3D images, and (d) volume of an ND10 microgel in the absence of NaIO<sub>4</sub> at 30 °C. The structural changes did not occur, indicating that the imaging process did not significantly affect the degradation of the microgels.



**Fig. S5.** Time dependence of the (a) height images, (b) phase images, (c) 3D images, and (d) volume of the NB10 microgel in the presence of 62.5 mM NaIO<sub>4</sub> at 30 °C. The results show that degradation of the microgels is caused by cleavage of the cross-linker.



**Fig. S6.** Time dependence of height images, phase images, and 3D images obtained from the HS-AFM analysis during the degradation of ND10 at 25 °C in the presence of 62.5 mM NaIO<sub>4</sub>: (a) Wide-range imaging and (b) single-particle imaging; (c) volume changes of a single microgel and (d) cross-sectional profiles corresponding to the red line in (b).



**Fig. S7.** Time dependence of (a) height images, (b) phase images, (c) 3D images, (d) volume, and (e) cross-sectional profiles corresponding to the red line in (a) for a single ND10 microgel during degradation in the presence of 62.5 mM NaIO<sub>4</sub> at 35 °C.



**Fig. S8.** Confirmation of reproducibility for a single ND10 microgel degradation behavior in the presence of 62.5 mM NaIO<sub>4</sub> at 35 °C. Time dependence of (a) height images, (b) 3D images, (c) volume, and (d) cross-sectional profiles corresponding to the red line in (a).



**Fig. S9.** The effect of cross-linking density of ND microgels on the degradation behavior. Time dependence of (a) height images, (b) phase images, (c) 3D images, (d) volume, and (e) cross-sectional profiles corresponding to the red line in (a) for a single ND5 microgel (swelling ratio = 11) during degradation in the presence of 62.5 mM NaIO<sub>4</sub> at 25 °C. It should be noted that ND microgels with higher cross-linking density were not obtained; ND15 microgels were aggregated during polymerization.



Fig. S10. Confirmation of reproducibility for a single ND10 microgel degradation behavior in the presence of  $62.5 \text{ mM NaIO}_4$  at 40 °C. Time dependence of (a) height images, (b) phase images, (c) 3D images, (d) volume, and (e) cross-sectional profiles corresponding to the red line in (a).

**Movie S1.** Height movie of ND10 microgels during degradation at 30 °C. The NaIO<sub>4</sub> concentration was 62.5 mM.

**Movie S2.** Height movie of the degradation of a single ND10 microgel at 30 °C. The NaIO<sub>4</sub> concentration was 62.5 mM.

**Movie S3.** Height movie of the degradation of a single ND10 microgel at 25 °C. The NaIO<sub>4</sub> concentration was 62.5 mM.

**Movie S4.** Height movie of the degradation of a single ND10 microgel at 35 °C. The NaIO<sub>4</sub> concentration was 62.5 mM.

**Movie S5.** Height movie of the degradation of a single ND10 microgel at 40 °C. The NaIO<sub>4</sub> concentration was 62.5 mM.