Supporting Information

The Deformation of Hydrogel Microspheres at the Air/Water Interface

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Experimental Procedures

Materials

N-isopropyl acrylamide (NIPAm, 98%), glycidyl methacrylate (GMA, 95%), *N*,*N*'-methylenebis(acrylamide) (BIS, 97%), 2,2'-azobis(2-methylpropinamidine) dihydrochloride (V-50, 95%), potassium peroxodisulfate (KPS, 95%), sodium chloride (NaCl, 99.5%), Rhodamine 6G (R6G), and 3-mercaptopropane sulfonic acid (MPSA) were purchased from Wako Pure Chemical Industries and used as received. Acrylic acid (AAc, 99%) was purchased from Sigma Aldrich and used as received. The $Ru(bpy)_3$ monomer (4-vinyl-4'-methyl-2,2'-bipyridine)bis(2,2'bipyridine)ruthenium(II)bis(hexafluorophosphate) was synthesized according to a previously reported procedure.[1] Distilled and ion-exchanged (EYELA, SA-2100E1) water was used in all experiments.

Synthesis of microgels by a modified aqueous precipitation polymerization

Poly(NIPAm-*co*-AAc) core–shell hydrogel microspheres (pNA microgels) (size > 6 μm) were prepared via a modified aqueous precipitation polymerization technique (**Scheme S1**). The polymerization was performed in a three-necked round-bottom flask (200 mL) equipped with a mechanical stirrer, a condenser, and a nitrogen gas inlet. Typically, the NIPAm monomer (0.6 g), AAc comonomer (63.2 μL), and cross-linker BIS (0.0098 g) were dissolved in deionized water (55 mL). The monomer solution was heated to 40 °C under a stream of nitrogen and constant stirring (250 rpm). The solution was sparged with nitrogen for a period of at least 30 min in order to remove any dissolved oxygen. Subsequently, the free-radical polymerization was initiated with KPS

(0.055 g) dissolved in deionized water (1 mL). Immediately after the initiation, the temperature was increased from 40 °C to 60 °C using a temperature gradient of 1 °C/3 min. Thereafter, a mixture of NIPAm monomer (3.5 g), AAc comonomer (875 µL), cross-linker BIS (pNA(1.4): 0.0927 g or pNA(2.7): 0.1855 g), and NaCl (0.0204 g, 10 mM) dissolved in deionized water (35 mL) was added to the reaction mixture at a feeding rate of 0.1 mL/min using a syringe pump. After 5 h, the feeding was stopped, and the reaction was stirred for 2 h at 60 °C, after which the microgel dispersion was cooled in an ice bath to stop the polymerization. The obtained microgels were purified twice by centrifugation/re-dispersion in water using a relative centrifugal force (RCF) of 20,000 g to remove unreacted reagents and other impurities. Similar to the synthesis of pNA microgels, pure pNIPAm microgels (both positively and negatively charged), poly(NIPAm-*co*-GMA) microgels, and poly(NIPAm-*co*-Ru(bpy)$_3$) were prepared via this modified aqueous precipitation polymerization. **Table S1** summarizes the details for the polymerization and **Figure S1** shows the optical microscopy images and chemical composition of these microgels.

Characterization of the microgels

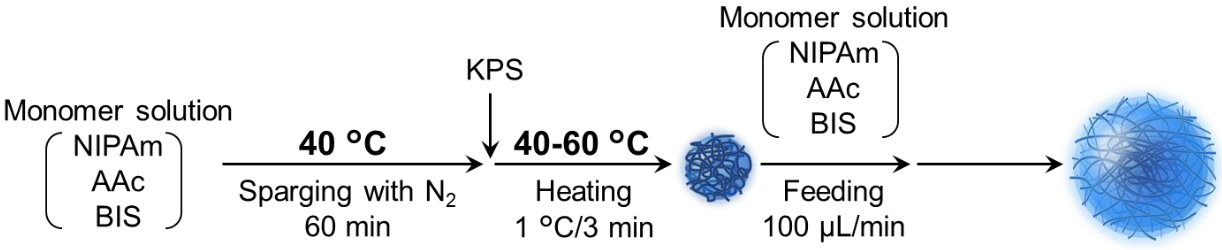
Microgels in aqueous solution were observed with an optical microscope (BX51 or BX53, Olympus) equipped with a fluorescence system (ramp: U-RFL-T, excitation: 460-495 nm, emission: 510 nm) and a digital camera (ImageX Earth Type A-5.0M Ver. 3.0.4, Kikuchi-Optical Co., Ltd.) or high-speed camera (AX50 2SA, Photron). Note that the images shown in **Figure 4** were observed with an optical microscope (Axio Scope. A1, Zeiss) equipped with a fluorescence system (ramp: HBO-100, excitation: 450-490 nm, emission: 510 nm) and a digital camera (ImageX Earth Type S-2.0M Ver. 3.1.3, KikuchiOptical Co., Ltd.). These fluorescence systems were used to excite the fluorescent dye Rhodamine 6G. The microgels were transferred into rectangular Vitrotube borosilicate capillaries (0.1 × 2.0 mm) by capillary action. In order to observe the microgels in detail, colloidal crystals of the microgels were obtained through a thermal annealing process at a concentration close to the critical concentration.

Dye labeling experiments

After labeling the obtained pNIPAm-based microgels with ~0.0001 wt% R6G at a microgel concentration of ~0.003 wt%, the samples were purified via centrifugation/re-dispersion in water using a relative centrifugal force (RCF) of 20,000 g to remove any excess R6G. The samples were observed by fluorescence microscopy.

Calculation of the critical concentration

The intrinsic viscosity ($[\eta]$) of each microgel at 25 °C was evaluated from the viscosity of sufficiently diluted dispersions measured with an Ubbelohde viscometer. As it is customary when dealing with microgels, the apparent volume fraction of the microgels (ϕ_{eff}; $\phi_{\text{eff}} \equiv c[\eta]/2.5$) was employed as a simple measure of the degree of packing, although ϕ_{eff} deviates from the real volume fraction in the concentrated regime where the microgels undergo deformation, deswelling, and interpenetration. The critical concentration, C^*, was a concentration of $\phi_{\text{eff}} = 1$.



Scheme S1. pNA core–shell microgels prepared via a modified aqueous precipitation polymerization.

Table S1. Chemical composition and diameter of the pNIPAm-based microgels developed in this study

Code	Core monomer			Shell monomer					Temp. (°C)	Initiator		Diameter (N = 50)	
	NIPAm (mol%)	BIS (mol%)	AAc (mol%)	NIPAm (mol%)	AAc (mol%)	GMA (mol%)	Ru(bpy)$_3$ (mol%)	BIS (mol%)		KPS (mM)	V-50 (mM)	in a rectangle capillary (μm)	at the air/water interface (μm)
pNA(1.4)	84	1	15	69.7	28.9	-	-	1.4	40→60	3.6	-	6.3 ± 0.4	20 ± 2
pNA(2.7)	84	1	15	68.8	28.5	-	-	2.7	40→60	3.6	-	4.2 ± 0.1	7.9 ± 0.2
pN/KPS	99	1	-	99	-	-	-	1	35→60	3.6	-	2.5 ± 0.2	3.4 ± 0.1
pN/V-50	99	1	-	99	-	-	-	1	40→60	-	3.6	2.5 ± 0.1	3.5 ± 0.2
pNG	99	1	-	69	-	27	-	4	40→60	-	3.6	2.0 ± 0.1	2.4 ± 0.1
pNG-MPSA*	-	-	-	-	-	-	-	-	-	-	-	4.1 ± 0.2	4.9 ± 0.1
pNRu	99.9	0.1	-	94.7	-	-	3.7	1.6	40→60	-	3.6	4.3 ± 0.3	10 ± 1

*pNG-MPSA microgels were prepared from pNG microgels according to a previous report.[2] Briefly, a mixture of pNG microgels (0.5 g), MPSA (ten times the amount of epoxy groups in the pNG microgels), and water (45 g) was poured in a 100-mL glass vial with stirring at room temperature, and the pH was adjusted to 11 with 1 M NaOH. The reaction was continued for 24 h. The obtained pNG–MPSA microgels were purified twice by centrifugation/redispersion in water using a relative centrifugal force (RCF) of 20,000*g* to remove impurities.

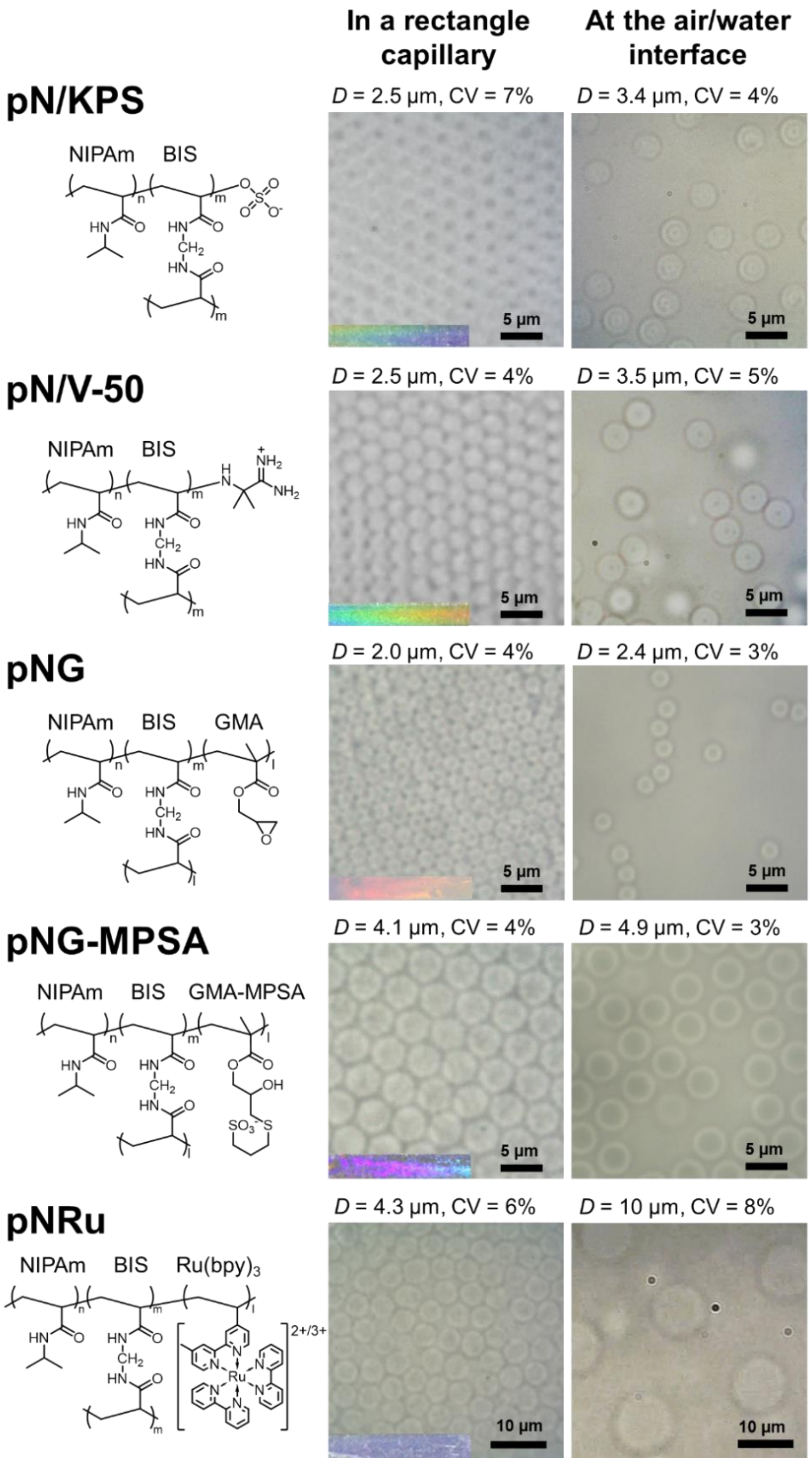


Figure S1. Optical microscopy images of different microgels. Inset photographs show colloidal crystals composed of each microgel. The microgels were observed in a rectangle capillary at high concentration (left column) and at the air/water interface (right column) of the dispersion droplets (N = 30). From these images, it is clear that these microgels are uniform, and that the applied synthetic method should be applicable to various pNIPAm-based microgels.

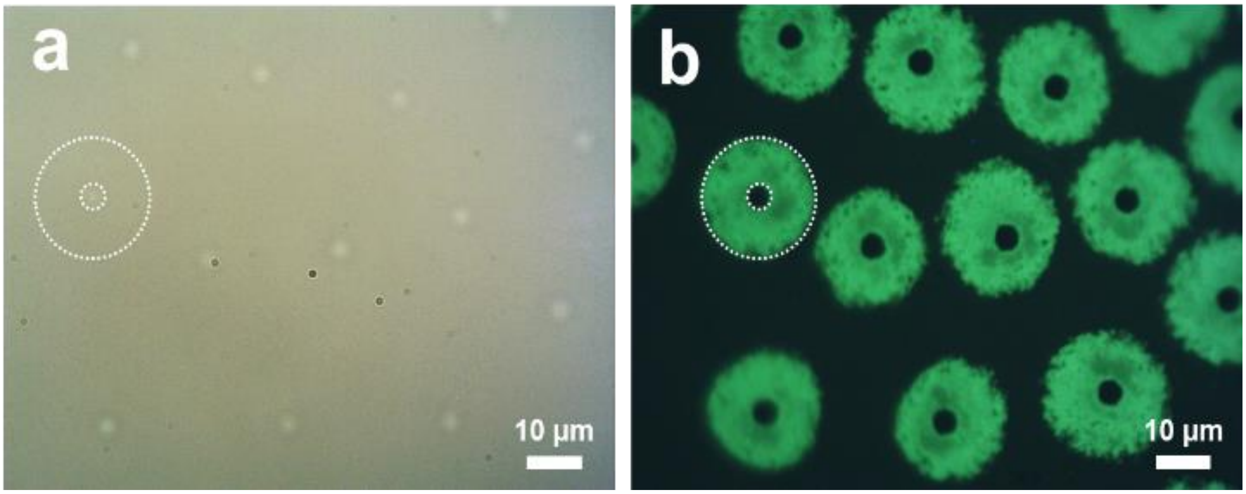


Figure S2. (a) Optical and (b) fluorescence microscopy images of the same pNA microgels after labelling with R6G dye molecules. The same area was observed at the air/water interface of the dispersion droplet at pH = 7 and 25 °C. The white dotted lines indicate the core part and the surface of an individual microgel.

Table S2. Deformation kinetic parameters of the pseudo-second-order model and parameter calculated from optical microscopy images of pNA(1.4) and pNA(2.7) microgels

Microgels	Plot parameters			Calculated parameter
	k_2 (µm^{-1} sec^{-1})	D_e (µm)	R^2	D_{ads}/D_{C*}
pNA(1.4)	2.74	20.1	0.9995	3.2
pNA(2.7)	10.4	4.43	0.9968	1.9

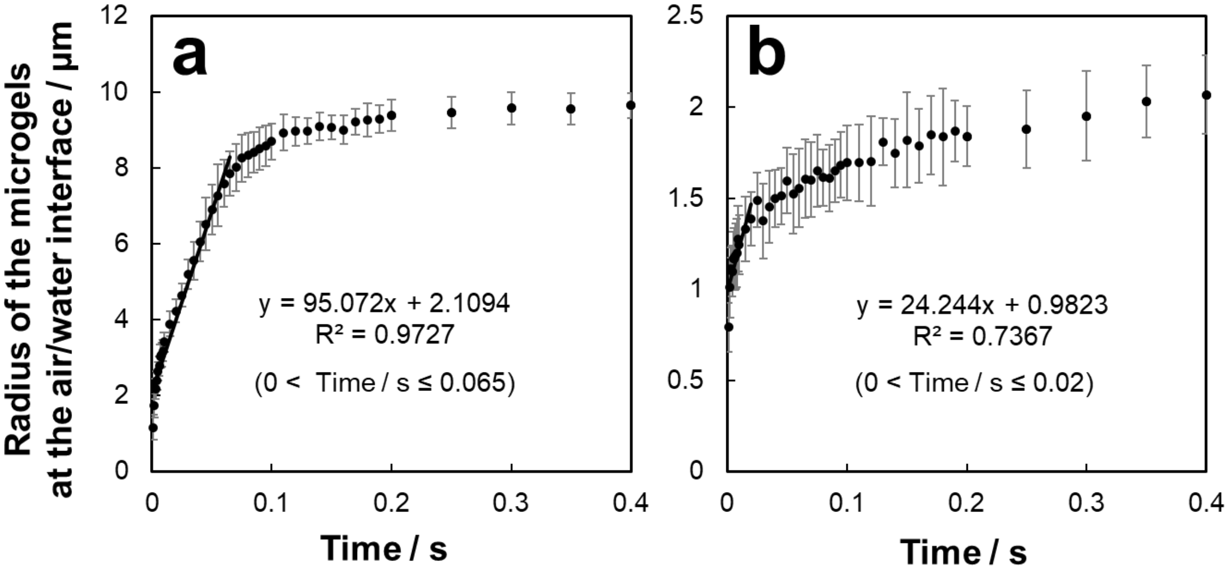


Figure S3. Radius of (a) pNA(1.4) and (b) pNA(2.7) microgels as a function of time at the air/water interface, which were calculated from the diameter (**Figure 2**).

Movie S1. Optical microscopy movie of pNA(1.4) microgels observed in a rectangle capillary.

Movie S2. Moment of adsorption and deformation of individual pNA(1.4) microgels at the air/water interface.

Movie S3. Moment of adsorption and deformation of individual pNA(2.7) microgels at the air/water interface.

REFERENCES

(1) P. K. Ghosh and T. G. Spiro, *J. Am. Chem. Soc.,* 1980, **102**, 5543-5549.
(2) D. Suzuki and H. Kawaguchi, *Colloid Polym. Sci.,* 2006, **284**, 1443-1451.