Multi-layer Core/Shell Microgels with Internal Complexity and their Nanocomposites

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Experimental Details

Materials

N-isopropyl acrylamide (NIPAm, purity 98%), *N,N′*-methylenebis(acrylamide) (BIS, 97%), styrene (99%), potassium peroxodisulfate (KPS, 95%), sodium dodecyl sulfate (SDS, 95%), methacrylic acid (MAc, 99%), fumaric acid (FAc, 98%), sodium chloride (NaCl, 99.5%), 1 mol/L and 0.1 mol/L sodium hydroxide solution (NaOH), and 0.1 mol/L hydrochloric acid (HCl) were purchased from FUJIFILM Wako Pure Chemical Corporation (Japan) and used as received. A 0.5% ruthenium-tetroxide (RuO_4)-stabilized aqueous solution was purchased from Electron Microscopy Sciences and used as received. For all experiments, water was distilled and then ion-exchanged (EYELA, SA-2100E1) before use.

Synthesis of CS microgels and composite CS microgels

CS microgels with multiple layers were synthesized *via* a one-pot aqueous free radical precipitation polymerization according to the conditions shown in **Table S1**. Initially, the core microgels were synthesized *via* a typical free-radical precipitation polymerization. An aqueous solution containing the monomers NIPAm and BIS was poured into a four-necked round-bottom flask equipped with a mechanical stirrer (250 rpm) and a reflux condenser. Subsequently, the monomer solution was heated to 70 °C in an oil bath, and the dissolved oxygen in the solution was removed by sparging with nitrogen for 30 min. Then, the initiator KPS (2 mM) dissolved in 2 mL of water was added to the monomer solution to start the polymerization. After 1 h, a shell-monomer solution was added to the reaction flask in order to prepare microgels with multiple layers. Several shell-monomer-solution additions were conducted, each 1 h after the previous addition. To evaluate the microgels as a function of polymerization time, at several time points during the polymerization, a 200 µL aliquot of the reaction solution was taken from the reaction flask. Throughout this manuscript, the CS microgels are denoted as C-S(*X*), where C and S refer to the core-microgel and shell layers, respectively, while *X* indicates the number of shell additions, as listed in **Table S1**.

To visualize the almost uncharged regions inside the CS microgels with multiple layers, soap-free seeded emulsion polymerization of styrene was performed in the presence of the microgels. 1 h after the final shell-monomer addition, hot water, which was heated to 70 °C and sparged with nitrogen for at least 30 min, was added to the flask to adjust the solid content to 0.17 wt.%. It should be noted here that, for the C-S(5) microgels, part of the obtained microgel dispersion was removed from the flask before adding hot water. After that, 1 M NaOH was added to the flask to adjust the pH of the system to ~10 in order to deprotonate the carboxyl groups inside the CS microgels. Then, styrene monomer was added to the flask. It is also noteworthy that for the C-S(5) microgels, the initiator KPS (1 mM) dissolved in 2 mL water was added to the flask before adding the styrene monomer. The polymerization was allowed to proceed for 24 h, and the resultant nanocomposite microgel dispersion was cooled to room temperature to stop the polymerization. To evaluate the microgels as a function of polymerization time, at several time points during the polymerization, a 200 µL aliquot of the reaction solution was taken from the reaction flask. The nanocomposite CS microgels were purified using two rounds of centrifugation (~10,000*g*, 15 °C) and redispersion in water.

Synthesis of CS microgels

CS microgels with a different amount of the 1st shell layer were synthesized *via* a one-pot aqueous free radical precipitation polymerization. Initially, the core microgels were synthesized *via* a typical free-radical precipitation polymerization. An aqueous solution containing the monomers NIPAm and BIS was poured into a four-necked round-bottom flask equipped with a mechanical stirrer (250 rpm) and a reflux condenser. Subsequently, the monomer solution was heated to 70 °C in an oil bath, and the dissolved oxygen in the solution was removed by sparging with nitrogen for 30 min. Then, the initiator KPS (2 mM) dissolved in 2 mL of water was added to the monomer solution to start the polymerization. After 1 h, a shell monomer solution (NIPAm, MAc, and BIS) was added to the reaction flask to prepare CS microgels. 1 h after the shell-monomer addition, the resultant microgel dispersion was cooled in an ice bath to terminate the polymerization. The resulting core and CS microgels were purified using two rounds of centrifugation (ca. 50,000*g*, 15 °C) and redispersion in pure water.

Synthesis of composite CS microgels

To visualize the almost uncharged regions inside the CS microgels with multiple layers, soap-free seeded emulsion polymerization of styrene was performed in the presence of the microgels. The polymerization protocols from our previous studies were followed.[1] Initially, water was poured into a 50 mL four-necked round-bottom flask equipped with a mechanical stirrer (250 rpm) and a reflux condenser. The flask was subsequently immersed in an oil bath and heated to 70 °C; dissolved oxygen was removed by sparging with nitrogen for 30 min. Subsequently, the purified CS microgel dispersion was added to the flask; the microgel concentration was adjusted to be 0.17 wt.% in 30 mL water. 1 M NaOH was added to the flask to adjust the pH of the system to ~10 in order to deprotonate the carboxyl groups inside the CS microgels. Then, the initiator KPS (0.0081 g, 1 mM) dissolved in 2 mL water was added to the reaction flask, and subsequently, styrene monomer was added to the flask to start the polymerization. The polymerization was allowed to proceed for 24 h, and the resultant nanocomposite microgel dispersion was cooled to room temperature to stop the polymerization. The nanocomposite CS microgels were purified using two rounds of centrifugation (~10,000g, 15 °C) and redispersion in water.

Scanning-electron-microscopy (SEM) characterization

Microgel morphologies in the dried state were visualized using SEM (JEOL Ltd., JCM-7000) and field emission (FE)-SEM (Hitachi Ltd., S-5000 or JEOL Ltd., JSM-IT800SHL). For the sample preparation, droplets of a dispersion of unpurified microgels were dried on a polystyrene substrate at room temperature. The sample substrates were sputtered with Pt/Pd prior to examination (15 mA, 6 Pa, 80 s).

Dynamic-light-scattering (DLS) measurements

The hydrodynamic diameters (D_h) of the core and CS microgels were determined *via* DLS using a Zetasizer NanoS and NanoZS (Malvern Instruments Ltd., UK). The D_h values were determined from the average values of three independent DLS measurements. The scattering intensity was detected at a total scattering angle of 173° in all cases. For the sample preparation, 1 mL of the diluted dispersions with 1 mM ionic strength were used, which was adjusted by using 0.1 M HCl solution to adjust the pH of solutions, as appropriate. The D_h value was calculated based on the measured diffusion coefficient using the Stokes–Einstein equation (Malvern, Zetasizer software v. 7.12).

Electrophoretic-mobility measurements

The electrophoretic mobility (μ) was measured using a Zetasizer NanoZS (Malvern, Zetasizer software v. 7.12). The sample-preparation procedure was identical to that for the DLS measurements. The μ values correspond to an average of 20 independent measurements, and the average of the results for three replicate measurements.

Transmission-electron-microscopy (TEM) characterization

The internal nanostructures of the CS microgels were characterized by preparing ultra-thin cross-sections. For that purpose, lyophilized nanocomposite CS microgels were stained for 30 min with RuO_4 vapor and then dispersed in epoxy matrices (EPON812, TAAB Laboratories Equipment). The matrices were heated at 70 °C for 24 h and then cut into ultrathin cross sections with a thickness of 100 nm using a microtome. The resulting samples were observed using TEM (JEOL JEM-2100 or JEOL JEM-1400Flash, operated at 80 kV).

Image analysis

ImageJ software (ver. 1.50) was used to determine the size and structures of the various microgels. The diameters of the microgels and polystyrene nanoparticles, as well as the number of polystyrene nanoparticles on the surface of the composite microgels, were calculated by analyzing the obtained images using ImageJ (N = 200). The coefficient of variation (CV) values was calculated as the following equation;

$$CV\ (\%) = \text{standard deviation} / \text{average value} \times 100$$

For the ultra-thin cross-sectional images, only images with errors within 200 nm of the average particle size determined using SEM were measured, considering that these ultra-thin cross-sectional images are 2D images of 3D particles.

Results and Discussion

Table S1. Chemical composition of CS microgels with a different number of shell layers

Code	core			1st shell addition			2nd shell addition		
	monomer	[mol.%]	[g]		[mol.%]	[g]		[mol.%]	[g]
	NIPAm	93.7	0.230	NIPAm	75	0.386	NIPAm	85	0.135
				MAc	20	0.078	FAc	10	0.016
C-S(2)	BIS	6.3	0.021	BIS	5	0.035	BIS	5	0.011
	water		50	water		10	water		10
	NIPAm	93.7	0.230	NIPAm	75	0.580	NIPAm	75	0.966
				MAc	20	0.118	MAc	20	0.196
C-S(5)	BIS	6.3	0.021	BIS	5	0.053	BIS	5	0.088
	water		50	water		10	water		20

| 3rd shell addition			4th shell addition			5th shell addition		
	[mol.%]	[g]		[mol.%]	[g]		[mol.%]	[g]
NIPAm	75	1.352	NIPAm	75	1.739	NIPAm	85	0.208
MAc	20	0.275	MAc	20	0.353	FAc	10	0.025
BIS	5	0.123	BIS	5	0.159	BIS	5	0.017
water		163	water		137	water		20
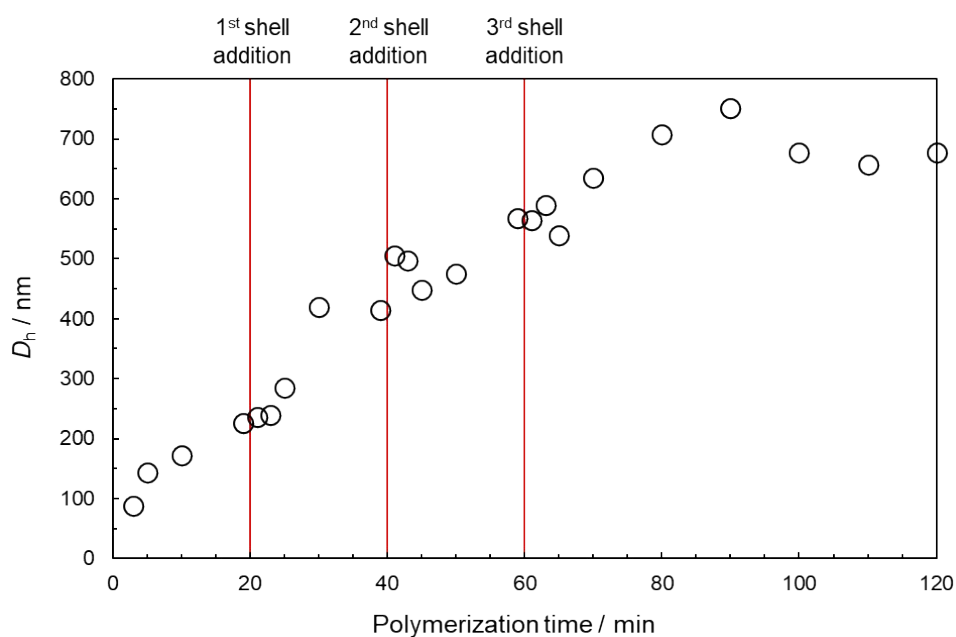
Figure S1. D_h of the CS microgels as a function of the polymerization time, as determined using DLS at pH = 3 and 25 °C. The shell-monomer mixture including MAc was added to the reaction flask after 20 min and 40 min, and that including FAc was added after 60 min.
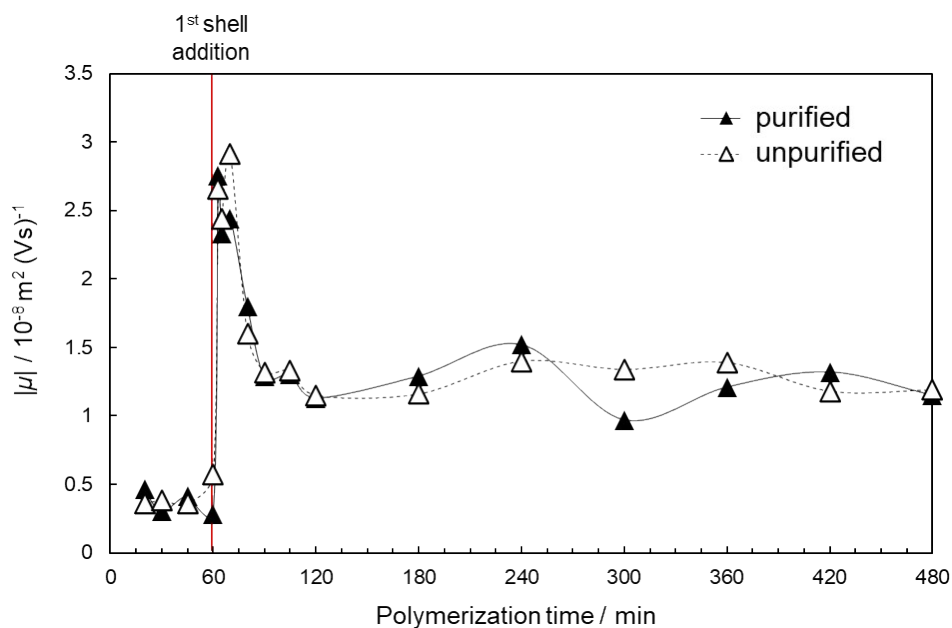
Figure S2. Absolute values of μ for the CS microgels (core – 1st shell) upon the addition of the first shell monomer mixture (NIPAm, MAc, and BIS) 60 min after the initiation of the core polymerization. The unpurified microgels and microgels purified using centrifugation were evaluated using ELS at pH = 11 and 25 °C. It should be noted here that μ shows negative values due to the presence of residues of the initiator and MAc.
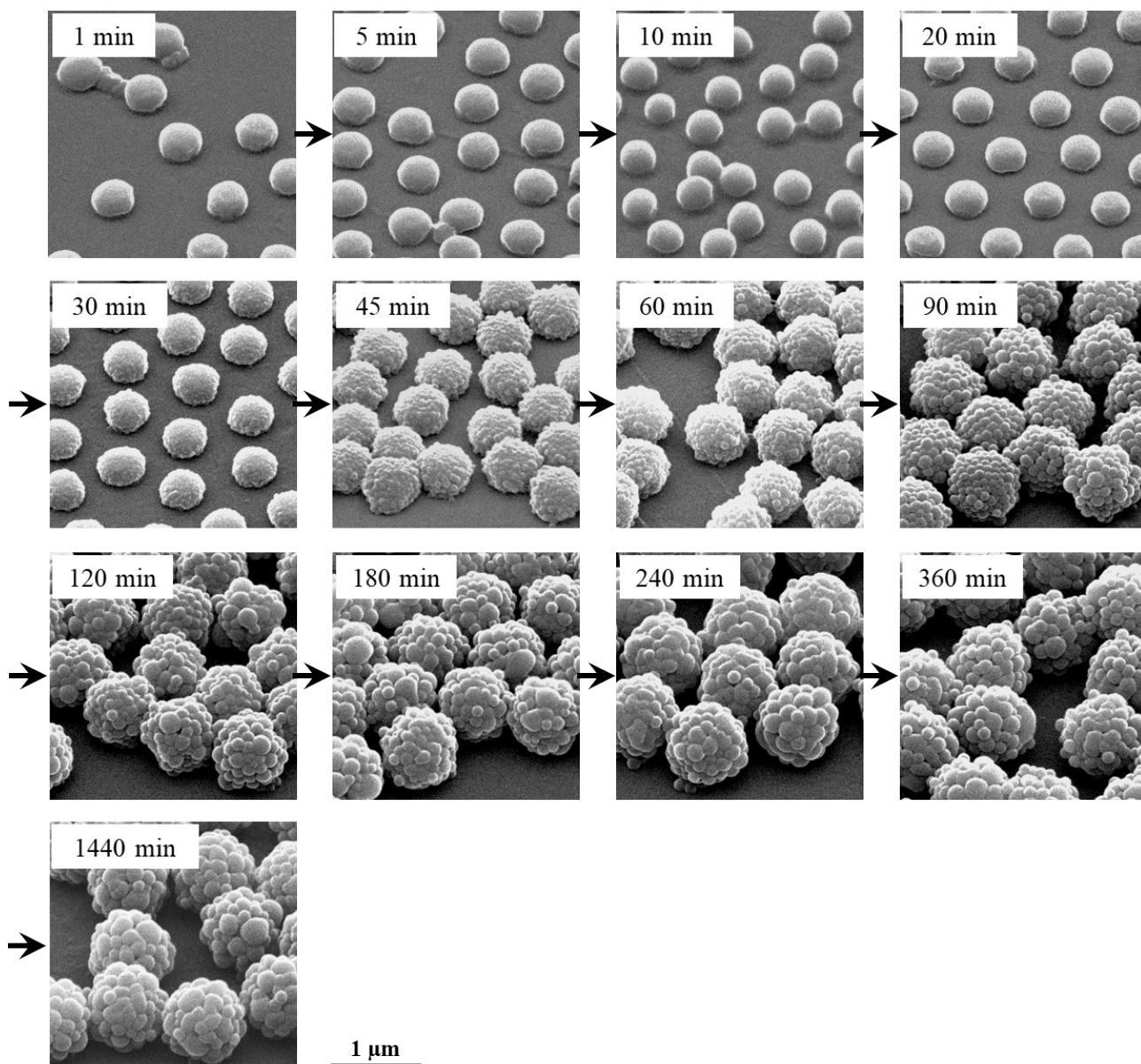
Figure S3. Time dependence of the morphology of the composite C-S(2) microgels during soap-free seeded emulsion polymerization after the addition of the styrene monomer, as observed using FE-SEM.
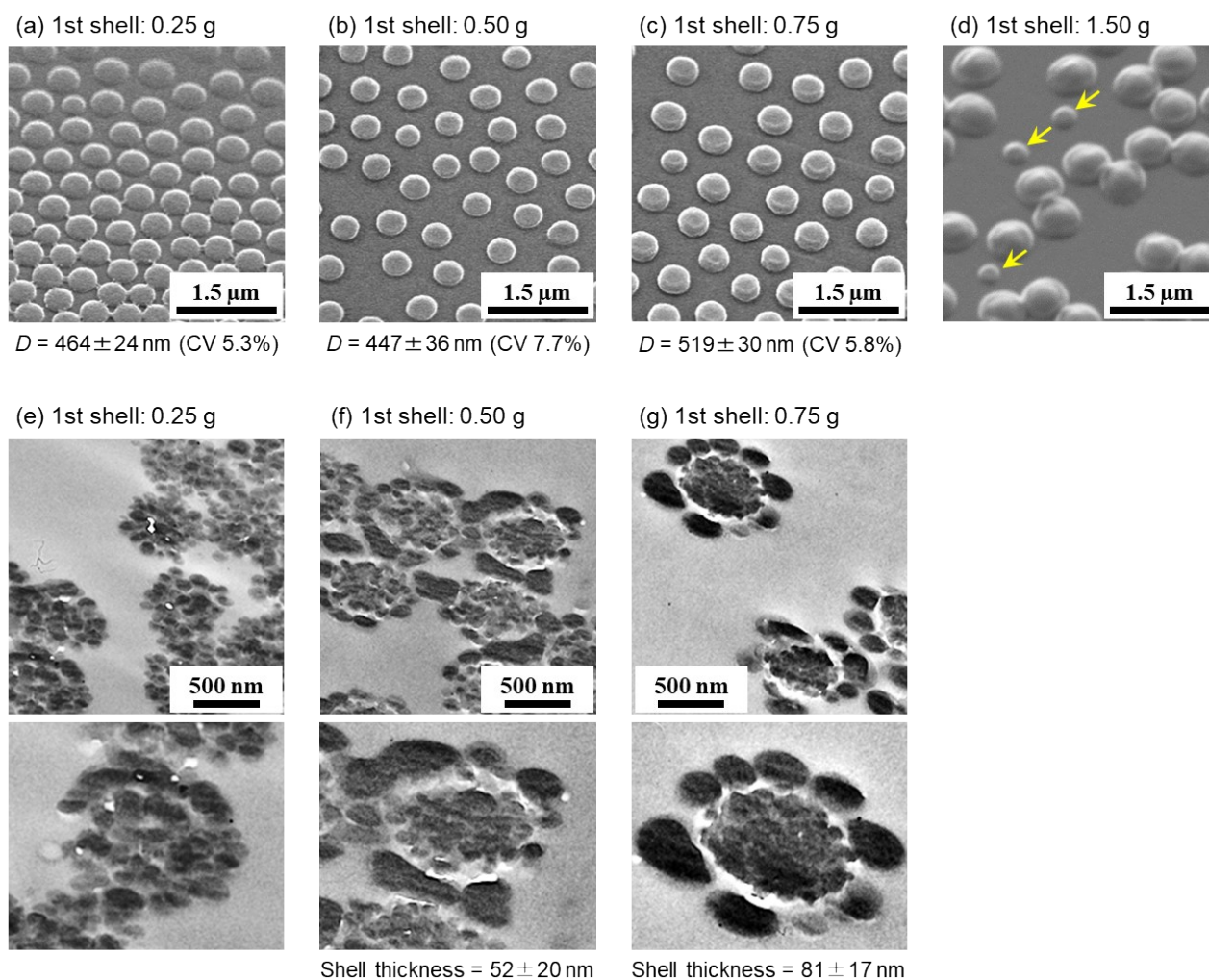
Figure S4. (a)–(c) FE-SEM and (d) SEM images of CS microgels (core – 1st shell) with a different amount of 1st-shell monomer during seeded precipitation polymerization. (a)–(c) The diameter, D, of microgels increases with the amount of the added 1st shell monomer; however, (d) secondary particles are formed (yellow arrows) when 1.5 g of the shell monomer was added, indicating that the shell monomer was not effectively introduced into the pre-existing core particles. (e)–(g) TEM images of ultra-thin cross-sections of composite CS microgels. These images show that the thickness of the polyelectrolyte layer, where the hydrophobic polystyrene nanoparticles was not composited, increases with increasing amount of the 1st shell monomer.

References

[1] Suzuki, D.; Horigome, K.; Kureha, T.; Matsui, S.; Watanabe, T. *Polym. J.* 2017, **49**, 695–702.