Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Self-Pulsation Observed in pH-Sensitive Microcapsules

Takayuki Narita*, Hirokazu Takakura, Naoko Ogata, Hidetaka Kawakita and Yushi Oishi

Department of Chemistry and Applied Chemistry, Saga University 1 Honjo, Saga, Japan

Contents

· Experimental Details

Preparation of PL oligomer-encapsulating PPL microcapsules: L-lysine-*alt*-terephthalic acid oligomer-encapsulating poly(L-lysine-*alt*-terephthalic acid) microcapsules (precipitate-encapsulating microcapsules) were prepared by an interfacial polymerization method. Ten milliliters of 1.5 M L-lysine aqueous solution containing 1.0 M sodium carbonate, where the pH 10.0, were dispersed in 100 ml of an organic solution containing 1%(v/v) of sorbitan trioleate to yield a W/O emulsion by stirring with a magnetic stir bar for 10 min; Sorbitan trioleate was used as a surfactant to stabilize the W/O emulsion. The organic solution consists of cyclohexane and chloroform (3:1 v/v). After stirring the solution, the polymerization was initiated by adding 100 ml of 0.1 M terephthaloyl dichloride solution. The mixture was stirred for 90 min at 5 °C. To stop the reaction and remove the unreacted terephthaloyl dichloride and the reaction residues that had leaked out from the capsules, the polymerized capsules were washed by decantation three times with cyclohexane and dried in air for 3 hours. Figure S3 shows size distribution of the obtained PL-oligomer encapsulating PPL microcapsule in distilled water.

Microscopic Observation: Five types of HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer solution were prepared with different pH values. These solutions were adjusted to pH 6.7, 6.9, 7.1, 7.3 and 7.5 with NaOH and ionic strength 0.01mol/l. Before the microcapsules were immersed in the buffer solutions, we randomly chose 25 of prepared dried capsules with an average size of 0.5 ± 0.1 mm. After that, five of the chosen capsules were resuspended into 1 mL of each buffer solution. The volume change processes of these microcapsules at different pH values were monitored by a CCD camera (Q-IMAGING, QICAM FAST 1394) attached with microscope (Leica, DMI 4000 B). The resuspended microcapsule was then placed on the observation stage of microscope (Leica DMI3000 B, Leica, Solms, Germany) and magnified images of microcapsules in the were captured every 10 s for 2 h by a 10-bit camera (QImaging, Burnaby, BC, Canada) attached to the microscope. The Obtained images were analyzed using Image-Pro plus (version 7.0 ; Sharpstack; Media Cybernetics Inc., Silver Spring, MD). Experiments were carried out at the room temperature which was adjusted to 296 K using an air-conditioner.

Characterization of the precipitate in the core of microcapsule: For fourier-transform infrared spectroscopy (FT-IR) and size exclusion chromatogram (SEC), 10 ml of 0.1 w/w % resuspended microcapsule solution was adjusted to pH 7.5 with ionic strength 0.01mol/l and stood for 12 h at room temperature. We conformed by a microscopic observation that the resuspended microcapsules have no precipitate in the core after this treatment. This microcapsule dispersing solution was filtered through a filtering paper in order to separate

microcapsule membranes and membrane fragments; a white precipitate reappeared after the pH was adjusted to 4.5 by adding acetic acid. The filtered solutions were characterized by infrared spectroscopy (FT-IR, FT-IR-6100, JASCO) and size exclusion chromatogram (SEC, column: TSKgel G4000PWXL – Tosoh Co., pump: 515 HPLC Pump – Waters Co., detector: 2414 refractive index detector – Waters Co., recorder: C-R8A Chromatopac – Shimadzu Corp., mobile phase: water, flow rate: 1.0 mL/min).

For UV-Vis absorption measurements, 50mg of dried PPL microcapsule was resuspended in 50 ml of HEPES buffer solution which adjusted to pH 7.5 with ionic strength 0.01mol/l, and mixed by magnetic stirring. One ml of the resuspended microcapsule solutions were sampled at 1, 60, 180, 360, and 720 min. These samples were immediately filtered with same method as above. UV-Vis absorption spectra were carried out on a quartz cell (10 mm × 45 mm × 10mm, Tokyo Glass Kikai Co. Ltd) using an Ocean Optics USB2000 absorption spectrometer.

Study of release behavior: We immersed a dried PPL microcapsule in HEPES buffer solution adjusted to pH 7.2 with ionic strength 0.1mol/l, and the microcapsule settled to the bottom of a quartz cell (10 mm × 40 mm × 1.0 mm, Tokyo Glass Kikai Co. Ltd). Immediately after the capsule was located at the bottom, we monitored the time course of UV-VIS absorbance of the buffer solution of the microcapsule in order to evaluate the release behavior of PL oligomer from a PPL microcapsule. The microcapsule images are captured the underside of the quiz cell, whose underside is transparent. On the other hand, Light for UV-VIS spectroscopy was incident from the side of the quartz cell and was passed through just above the targeted microcapsule. The absorbance measured at 246 nm in every 2 seconds by Ocean Optics USB2000 absorption spectrometer.

· Legend of Supporting Video 1

The movie of PL oligomer enclosed in PPL microcapsules after immersion in the 10mM HEPES-NaOH (pH6.0) buffer solution. Viewing window is 3 mm across, and the video is 300 times faster than real time.

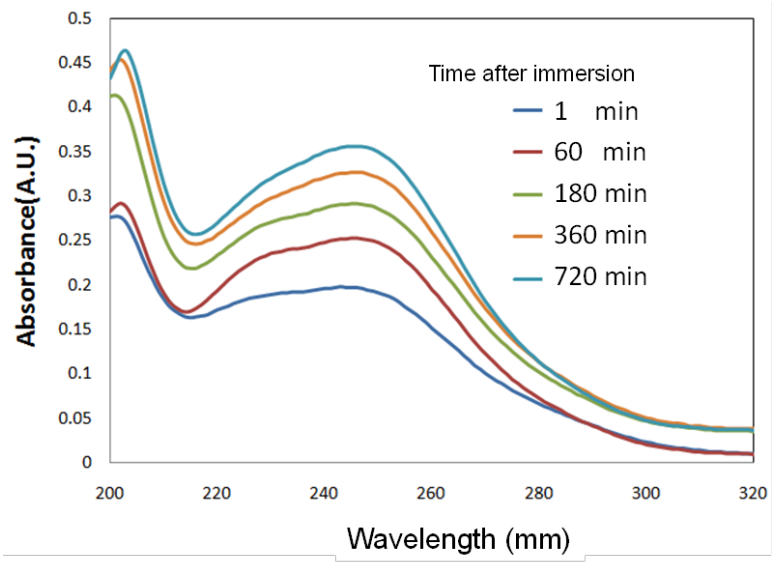

Figure S1. UV–VIS absorbance spectra of the filtered solutions, which were sampled at 1, 60, 180, 360, and 720 min from resuspended microcapsule suspension (0.1 w/w % of PL-oligomer encapsulating PPL microcapsule HEPES-NaOH solution, pH 7.5, ionic strength 0.01mol/l)

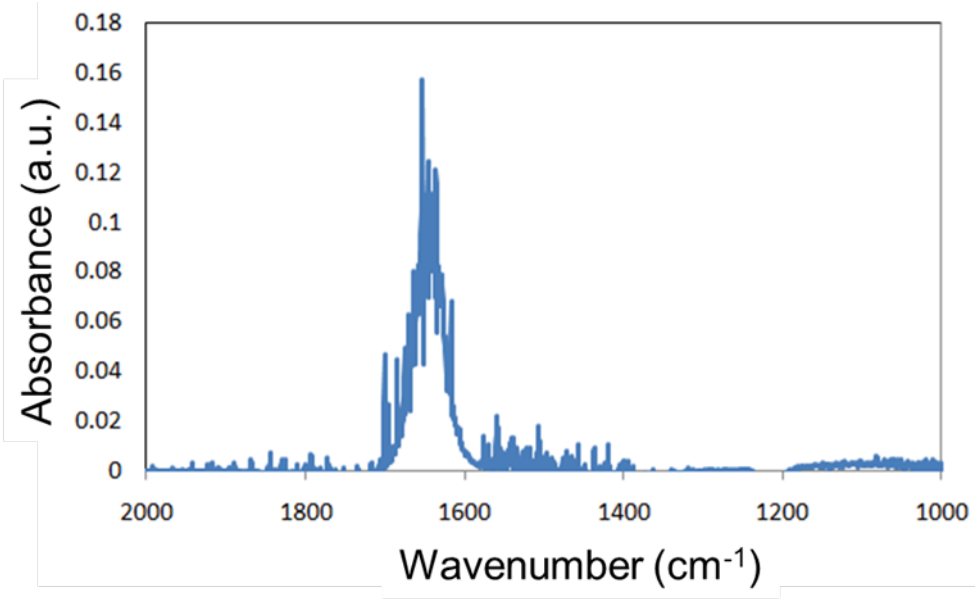

Figure S2. FT-IR spectrum of the filtered sample of HEPES-NaOH solution containing PL-oligomer encapsulating PPL microcapsule, which immersed into 1mM HEPES-NaOH (pH7.0) buffer solution for 12h

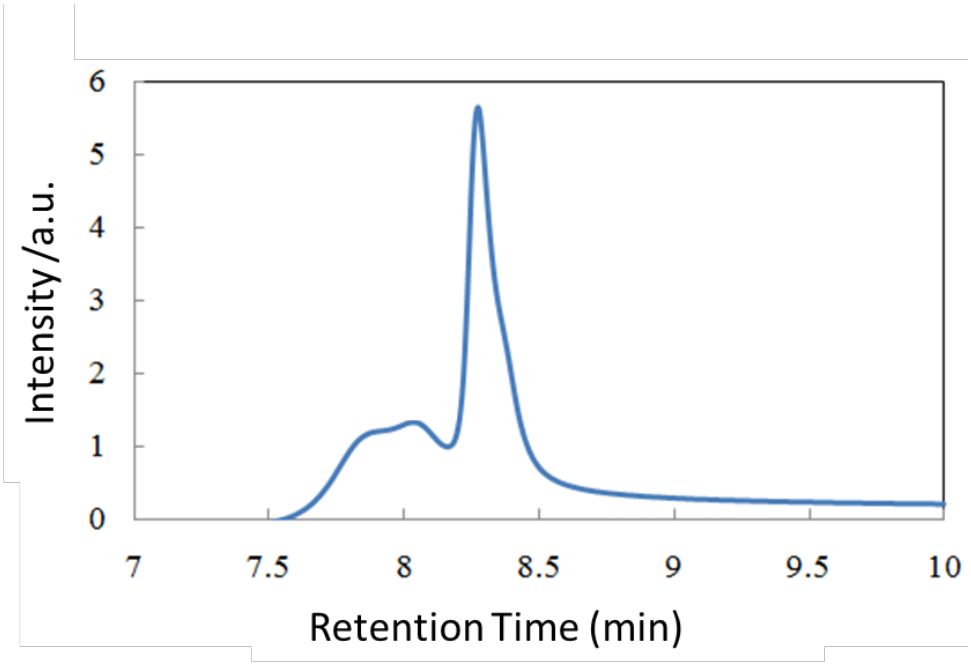

Figure S3. Size exclusion chromatogram of the released PL oligomer from PPL microcapsule. The HEPES-NaOH solution was obtained from the filtered sample of containing PL-oligomer encapsulating PPL microcapsule, which immersed into 1mM HEPES-NaOH (pH7.0) buffer solution for 12h.

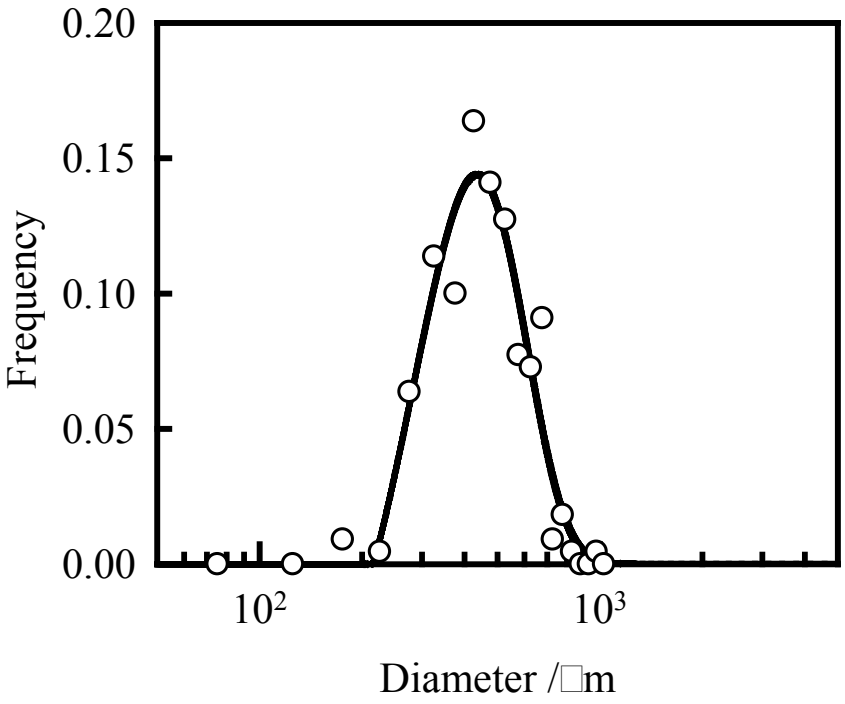

Fig. S4. Size distribution of the PL-oligomer encapsulating PPL microcapsule in water.