Supporting Information

Light-Induced Evolution of Microaggregates: Transformation to Vesicles, Cyclic Growth and Collapse and Vesicle Fusion

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Experimental Section

Synthesis of PGMA macro-CTA: PGMA macro-CTA was synthesized *via* conventional RAFT polymerization of GMA by using CTCPA as a chain transfer agent (CTA) and AIBN as an initiator. Typically, CTCPA RAFT agent (0.12 g, 0.4 mmol), GMA monomer (1.60 g, 10 mmol), and AIBN (0.013 g, 0.08 mmol) were dissolved in methanol (10 mL) in a schlenk flask and purged under N_2 for 30 mins. The sealed flask was immersed into an oil bath at 70 ^oC for 4 h. The reaction solution was then quenched in an ice bath and precipitated into glacial diethyl ether, followed by filtration. The product was dried under vacuum overnight and collected as a yellow solid.

PET-RAFT aqueous dispersion polymerization of PGMA-b-PHPMA: A typical protocol for the synthesis of $PGMA_{19}$-*b*-$PHPMA_{25}$ is as follows. $PGMA_{19}$ macro-CTA (0.021 g, 0.006 mmol), HPMA (0.022 g, 0.15 mmol) and $Ru(bpy)_3Cl_2 \bullet 6H_2O$ (1.5 μL, 10 ppm relative to monomer) were dissolved in water (1.72 g, 2.5 wt% solid content). The aqueous solution was transferred into a constant temperature quartz cell. The reaction solution was irradiated by blue light lamp (480 nm, 20.8 mW/cm^2) at 25 ^oC without deoxygenation, and the reaction was stopped by switching off the lamp. For polymerization kinetics study, aliquots were withdrawn at predetermined time and analyzed by ^1H NMR and GPC to determine monomer conversion, number-average molecular weight (M_n), weight-average molecular weight (M_w)

and polydispersity index (PDI, M_w/M_n). The theoretical molecular weight ($M_{n,th}$) was calculated based on the ^{1}H NMR results according to this equation: $M_{n,th} = ([M]_0/[\text{macro-CTA}]_0 \times \chi \times M_{monomer} + M_{n,\text{ macro-CTA}})$, where $[M]_0$, $[\text{macro-CTA}]_0$, χ, $M_{monomer}$, $M_{n,\text{ macro-CTA}}$ are initial monomer concentration, initial macro-CTA concentration, monomer conversion, molecular weight of monomer and molecular weight of macro-CTA, respectively.

Synthesis of rhodamine-labeled PGMA-b-PHPMA: Different amount of Rhodamine labeled-MA (0.29, 0.58, and 1.74 μg/g) was added with HPMA monomer at the beginning of the PET-RAFT polymerization. The reaction was stopped by turning off the blue light lamp.

^{1}H NMR spectroscopy: ^{1}H NMR spectra of samples in deuterated methanol (methanol-d_4) were recorded using an Agilent I500 NMR spectrometer.

Gel permeation chromatography (GPC): M_n, M_w and M_w/M_n of polymers were determined by GPC using an Agilent 1260 system equipped with a refractive index detector. The eluent was DMF with 0.05 M lithium bromide (LiBr) at a flow rate of 1.0 mL/min at 50 ^{o}C. Calibration curve was achieved using a series of monodispersed polymethylmethacrylate (PMMA) standards with a molecular weight ranging from 4600 to 1.5×10^6 (Agilent Technologies).

Optical and fluorescence microscopy: After irradiated by blue light for 4 h, the reaction solution was stopped by switching off the lamp. 50 μL reaction solution was transferred to a frame-seal chamber on a glass slide and fixed with a flexible plastic coverslip. For observation with fluorescence microscope, nile red (1 μg/g) or rhodamine 6G (4 μM) was mixed with the samples. The sample was observed with an inverted fluorescence microscope (Axio Observer A1, Zeiss) equipped with a fluorescence light source (X-Cite 120Q) and BD^{TM} CARV II confocal imager. The optical micrographs were recorded using a AxioCam and AxioVision software. The fluorescent micrographs were recorded using a CCD camera and a μManager software. Excitation filter (455-495 nm) and emission filter (500-545 nm) were selected for blue light channel, and excitation filter (540-590 nm) and emission filter

(600-650 nm) were used for green light channel, respectively. The micrographs were analyzed using ImageJ software and MATLAB. Since nile red can only be excited by green light, cycles of 5 s blue light and 100 ms of green light irradiation were used for irradiation and capturing photographs, respectively.

Transmission electron microscopy (TEM): The block copolymer solution (1%, 10 μL) was dropped onto a copper grid with formvar/carbon film (TED PELLA, INC) and blotted with filter paper to remove excess solution. The grids were then dried overnight and observed using a JEOL 2100 electron microscope at an acceleration voltage of 80 kV.

Movie S1. Evolution of microaggregates with rhodamine exposed to blue light for 30 mins.

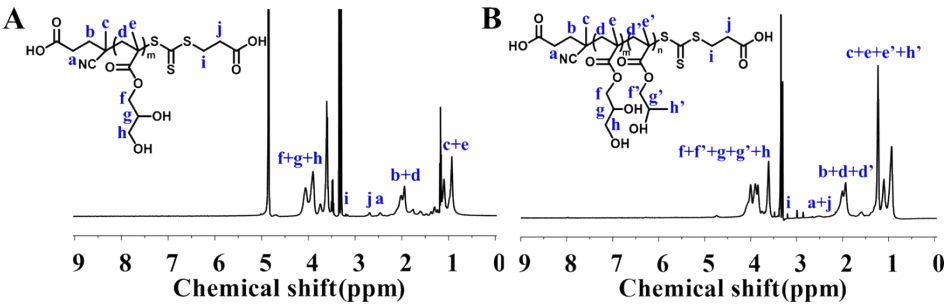

Figure S1. (A) ^{1}H-NMR spectrum of PGMA macro-CTA in methanol-d_4. (B) ^{1}H-NMR spectrum of purified G_{19}-H_{25} copolymer in methanol-d_4.

Since our aim was to obtain micron-sized objects, a short hydrophilic PGMA macro-CTA with target degree of polymerization (DP) of 25 was first synthesized *via* conventional RAFT polymerization of GMA (Figure 1). ^{1}H NMR and GPC results suggested the DP of PGMA macro-CTA was 19, and M_n and M_w/M_n were 10900 and 1.37, respectively (Figure S1A). Then, we prepared $PGMA_{19}$-*b*-$PHPMA_{25}$ copolymer (abbreviated as G_{19}-H_{25}) via PET-RAFT polymerization of HPMA with $PGMA_{19}$ macro-CTA as a stabilizer in an aqueous medium. $Ru(bpy)_3Cl_2$ was selected as a photoredox catalyst due to its high efficiency and good water solubility.

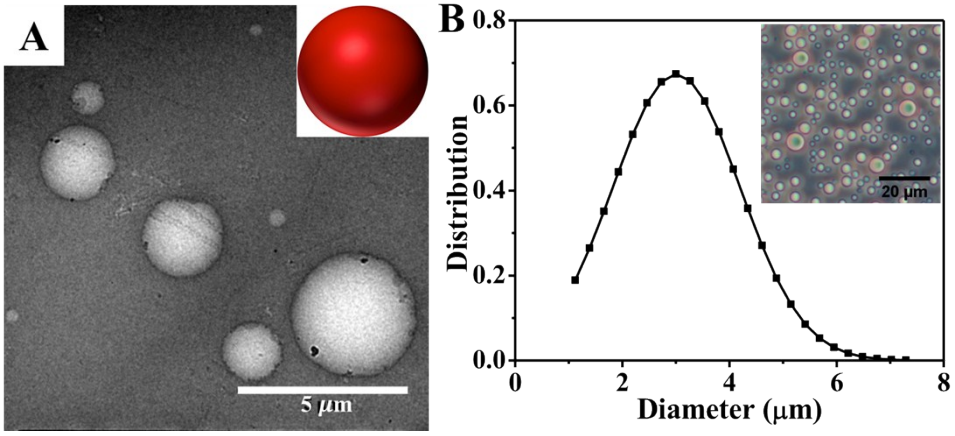

Figure S2. (A) TEM image of the microaggregates. The inset is a schematic view of the microaggregate. (B) Size distribution analyzed from the optical micrograph of G_{19}-H_{25} microaggregates.

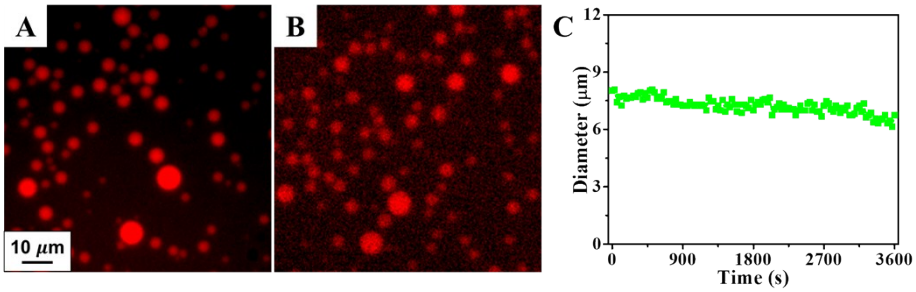

Figure S3. Fluorescence micrographs of G_{19}-H_{25} microaggregates with nile red before (A) and after (B) irradiating with green light for 30 mins.

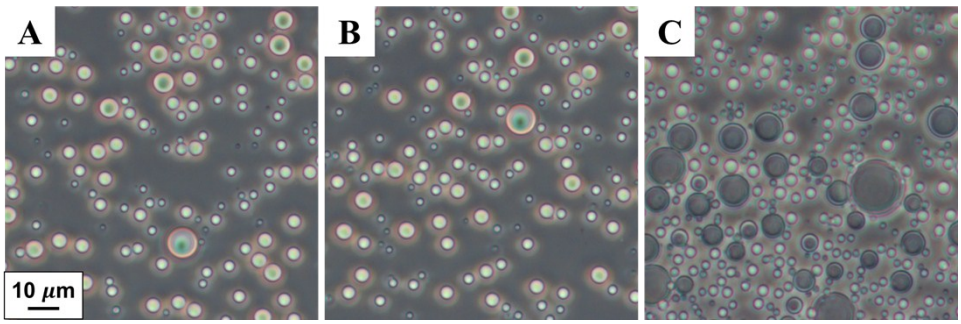

Figure S4. Optical micrographs of G_{19}-H_{25} microaggregates in the absence of dyes before (A) and after irradiating with green light (B) or blue light (C) for 30 mins.

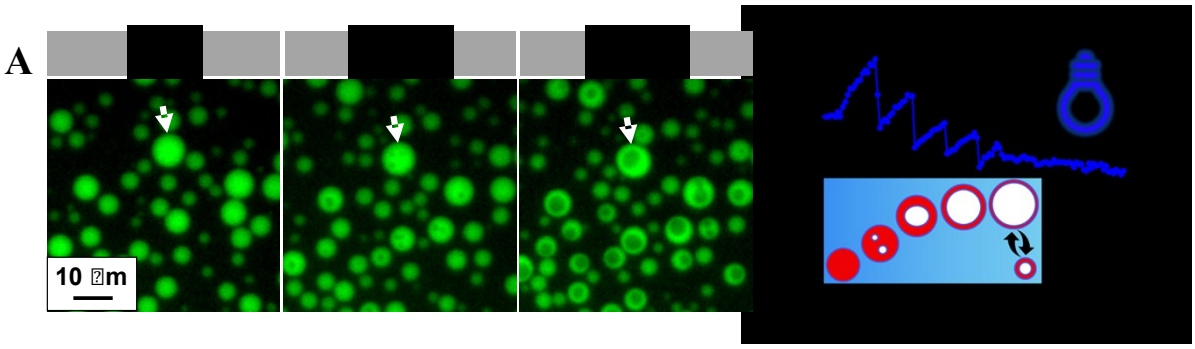

Figure S5. (A) Time sequence of fluorescent micrographs of G_{19}-H_{25} micro-objects with rhodamine 6g irradiated under blue light at different time. (B) Trace of diameter over time of the micro-objects marked in white arrows.

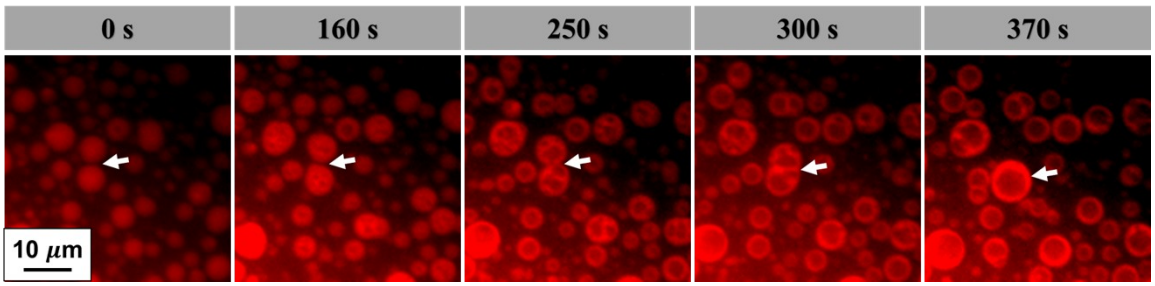

Figure S6. Time sequence of microaggregates-to-vesicles transformation, accompanying by fusion for the micro-objects (5%).

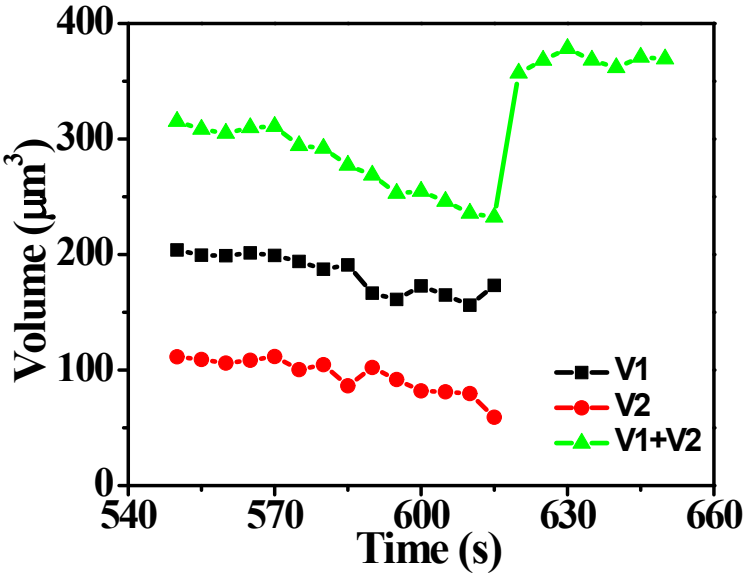

Figure S7. Variation of volume of fusing vesicles in Figure 4.

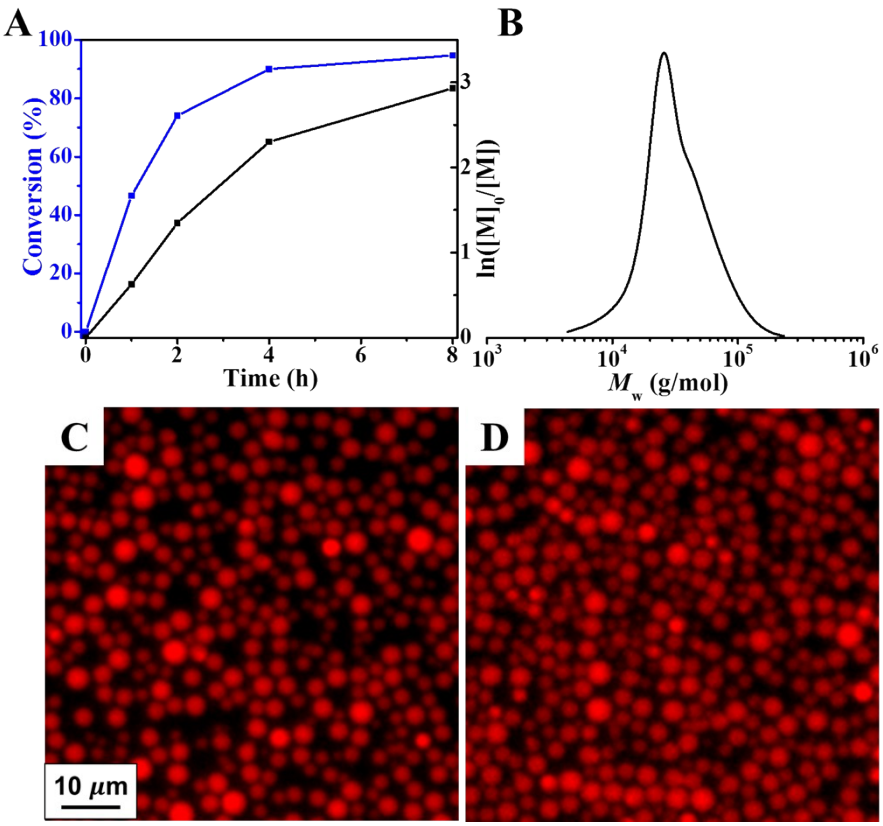

Figure S8. (A) Monomer conversion-time plots and ln ($[M]_0/[M]$)-time plots for the PET-RAFT aqueous dispersion polymerization of $PGMA_{19}$-*b*-$PHPMA_{50}$ copolymer. (B) GPC trace of $PGMA_{19}$-*b*-$PHPMA_{50}$ copolymer at 4h. Fluorescent micrographs of G_{19}-H_{50} micro-objects with rhodamine before (C) and after (D) irradiated by green light for 1h.