Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information

Controllable one-step double emulsion formation via phase inversion

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Experimental Section

PMMA adsorption test

The adsorption of PMMA at the water-toluene interface was investigated by measuring the interfacial tension using a pendant drop technique[1]. For this, a 10 μL-water droplet was produced at the end of a micro-syringe tip (OD=75 mm, Hamiltonian) that was immersed in the PMMA toluene solution at various concentrations from 0.001 to 10.0 wt%. Using a CCD camera (WAT-902H, Watec), images of the droplets were then recorded at time intervals of 1 minute. Finally, interfacial tension changes with time for each concentration of PMMA were obtained by analyzing the shapes of the droplets

The preparation of W/O/W double emulsion

HDK N20 silica particles, generously provided by Wacker Chemie, were initially dissolved in deionized water, and this aqueous solution was then subjected to a bath ultrasonicator for an hour at 25 ºC to prevent particle aggregation. PEI (poly ethylene imine, branched, M. W. = 25000 g/mol, Sigma Aldrich) was dissolved in deionized water as well. These silica nanoparticle suspension and polymer solution were placed in a glass vial with a soybean oil (Sigma Aldrich), and their volume ratios of the water phase were varied from 30% to 70% with 6mL of a total volume. The emulsification was carried out for 1 minute using a vortex machine (~3000rpm), and a small amount of Nile-red dye molecules (Sigma Aldrich, 10 μg/mL of concentration) were also added to the soybean oil for utilizing a fluorescence microscopy.

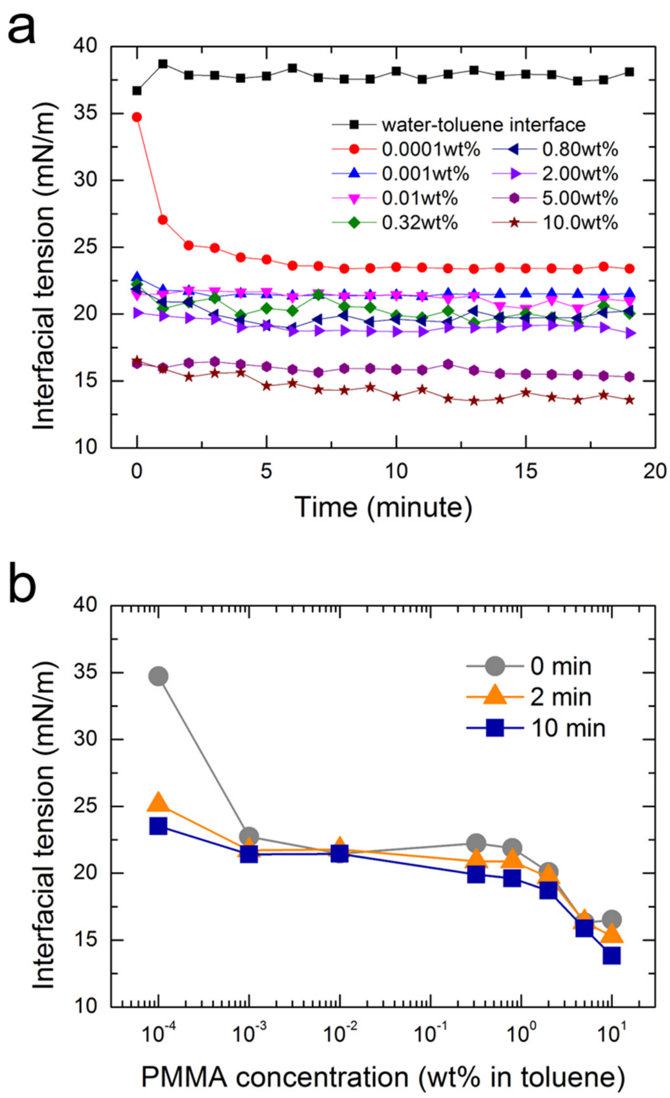

Fig. S1. (a) Interfacial tension of water/toluene interface at each concentration of PMMA in toluene was measured with time at 20 ℃ using the pendant drop technique[1]. The interfacial tension of bare water-toluene interface was found to be ~ 37 mN/m, which agrees well with the known value[2]. As the PMMA concentration increases, the interfacial tension decreases more, which indicates that the PMMA has quite strong interfacial activity. (b) Interfacial tension with various PMMA concentrations at 0 min (immediately after producing a water droplet in the PMMA solution), 2 min, and 10 min.

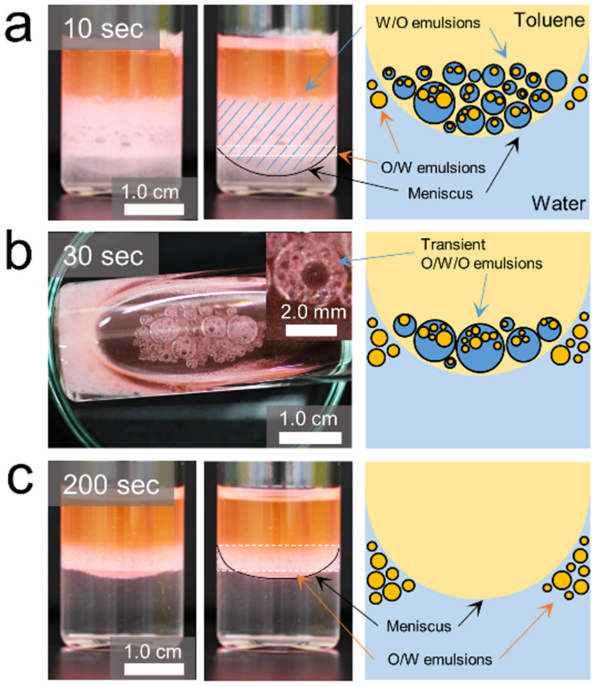

Fig. S2 (a-c) Time series photographs of emulsions after an emulsification (for very short time scale, <1 second), and cartoon depicting how to determine the type of the emulsions. Emulsions are solely stabilized by PMMA (0.80 wt% of toluene with Nile red at 10 μg/mL, and Φ_w=0.5). The type of emulsions is determined by the locus of droplets compared with the meniscus. Since the density of a water drop is larger than that of the continuous oil phase, W/O emulsion drops are dispersed above the meniscus. As time goes by, drops start to settle to the center of the meniscus, which is the lowest position for the dispersed phase, thereby clearly indicating that the turbid layer accumulated on the meniscus consists of the W/O emulsion drops. Due to a lower density of oil droplets, O/W emulsion drops, on the other hand, tend to move up, compared to the continuous water phase, and thus, they are placed in a gap between the meniscus and the glass vial wall. (a) At 10s after the short time emulsification, the thick emulsion layer located above the meniscus is expected to be a W/O emulsion (blue lines) while the thin band around the meniscus is speculated as an O/W emulsion (white box). (b) Photograph of transient O/W/O double emulsions taken 30 seconds after the short time (<1 second) emulsification and its magnified image. From the images, we could identify that the water droplets in W/O emulsions include small oil droplets inside, resulting in the O/W/O double emulsion morphology. (c) At 200 seconds after the short time emulsification (<1 second), there is the only thin band below the water-toluene meniscus, indicating an O/W emulsion.

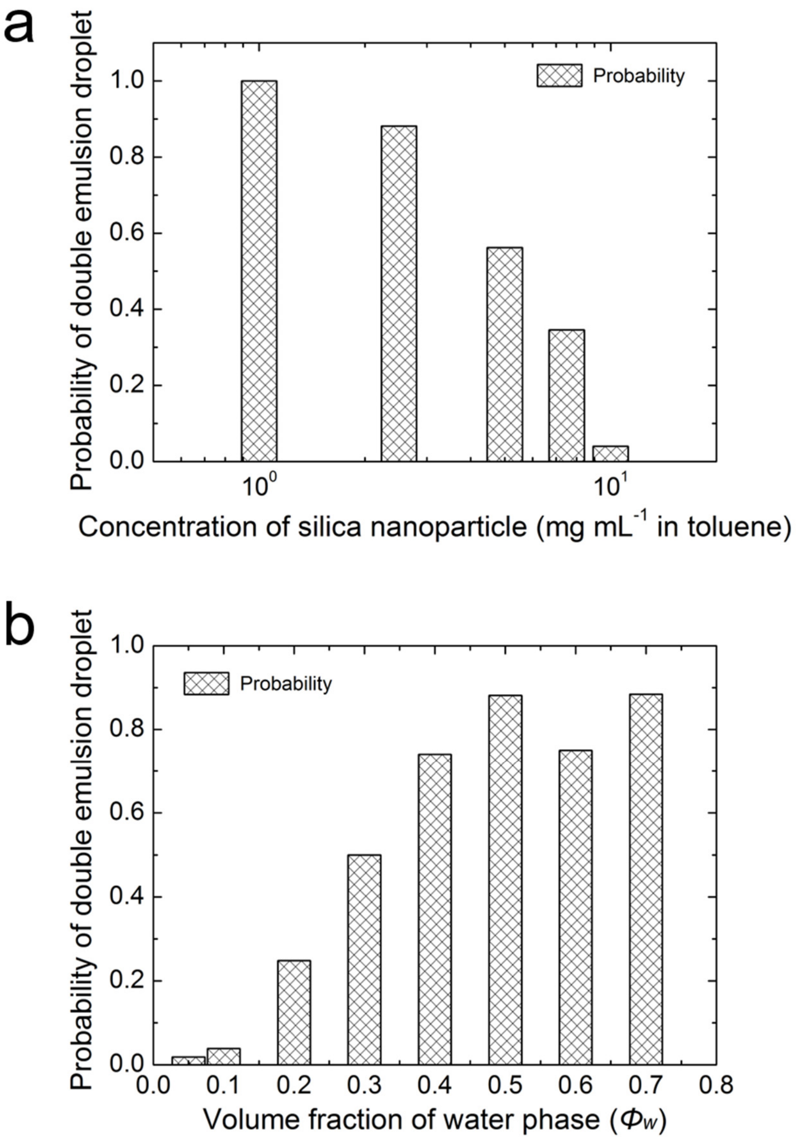

Fig. S3. Probability of double emulsion as a function of the particle concentration (a) and the volume fraction of water phase (b) with 0.8 wt% of a fixed PMMA concentration. Here, a probability of double emulsion corresponds to a number fraction of double emulsion droplets, compared to total outer droplets (O/W/O double emulsion droplets + W/O single emulsion droplets). Each fraction of double emulsion droplets was calculated by the micrographs of Fig. 4 and Fig. 5.

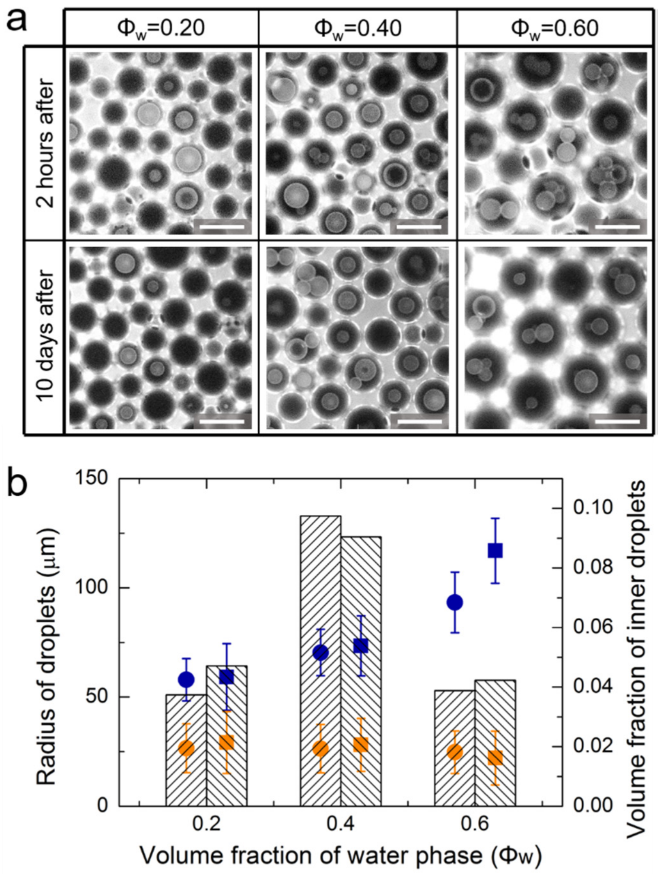

Fig. S4. (a) Fluorescent micrographs of the O/W/O double emulsions (2.5 mg/mL hydrophobic silica and 0.80wt% PMMA in toluene) with various water fractions 2 hours (1st row) and 10 days (2nd row) after the emulsification. Scale bars, 200 μm. (b) Comparison between radius of droplets (left axis) / volume fraction of inner droplets (right axis) 2 hours and 10 days after the emulsifications. Each blue symbol represents the radius of outer droplets after 2 hours (●) and 10days (■) while each orange symbol indicates the radius of inner droplets after 2 hours (●) and after 10 days (■), where the error bars denote the standard deviation of the distribution of each radius. Each volume fraction of the inner droplets after 2 hours (▨) and 10 days (▧) is shown with the bar. These results support the idea that there is no significant change of the radius of droplets or of the volume fraction of the internal phase for at least 10 days.

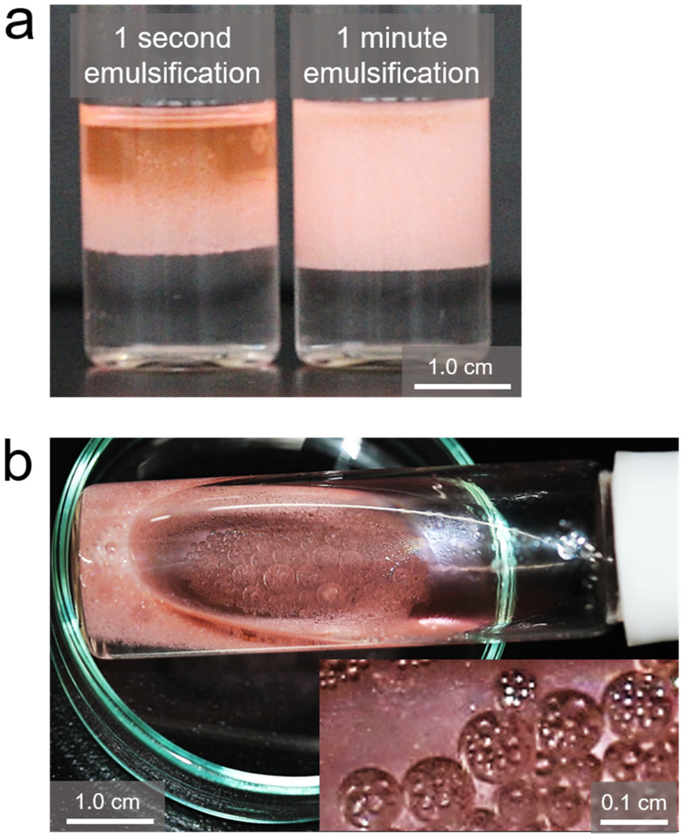

Fig. S5. Photographs of emulsion stabilized solely by Poly vinyl acetate that contains the carbonyl group in its molecular structure (0.50 wt% of toluene with Nile red at 10 μg/mL, Φ_w=0.5). (a) Photographs of two different emulsions taken 10 minutes after the short time (<1 second) and the long time (1 minute) emulsifications. The result indicates that the formation of O/W emulsion is accumulated as the mixing process is undergone. (b) Photograph of transient O/W/O double emulsions 30 seconds after the short time (<1 second) emulsification, and its magnified image. The transient O/W/O double emulsions were disappeared within a few minutes, which is very similar with the PMMA case, as indicated in Fig. S2b. This result strongly suggests that the early stage of emulsification that corresponds to the collision of droplets, could be governed mainly by polymer molecules, rather than silica particles, and the further adsorption of particle on the interface could stabilize the transient double emulsions.

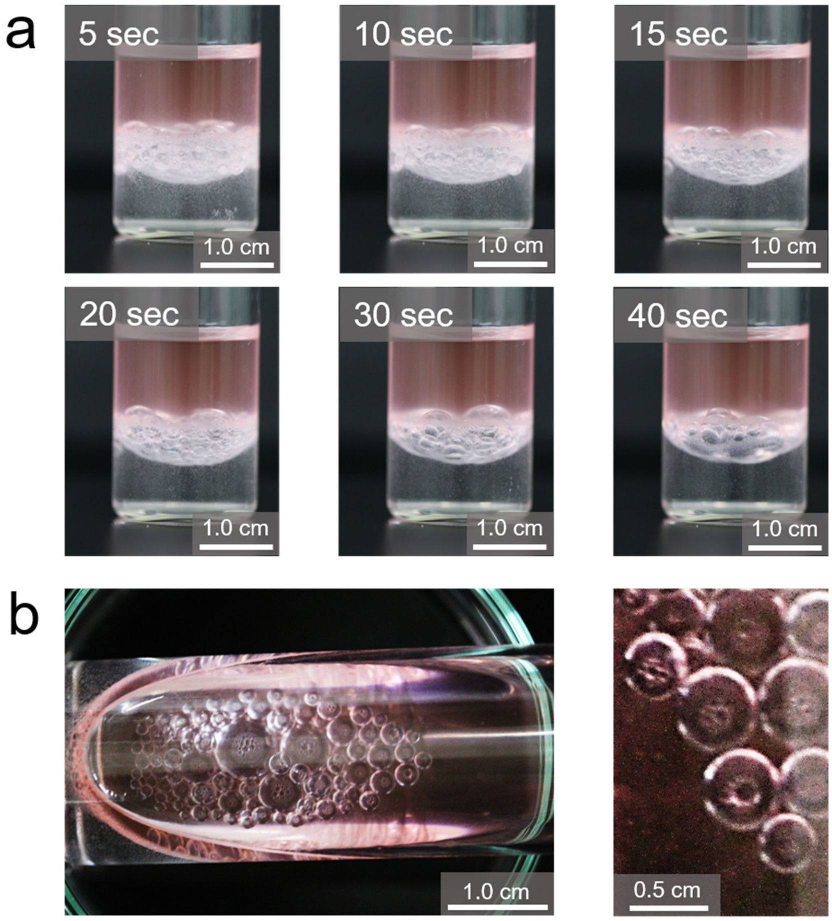

Fig. S6. Photographs of emulsion stabilized solely by Poly lactide that contains the carbonyl group in its molecular structure (0.10 wt% of toluene/benzene mixture with Nile red at 10 μg/mL, Φ_w=0.5). (a) Time-series photographs after the short time (<1 second) emulsification. Both W/O and O/W emulsions are produced initially, but neither of them was remained after a few minutes. Even for the long time emulsification of 1 minute, neither of emulsions survived because of their poor stability. (b) Photograph of transient O/W/O double emulsions taken 30 seconds after the short time (<1 second) emulsification and its magnified image. Also in this case, the transient double emulsions disappear within a few minutes, hence it is necessary to add hydrophobic silica nanoparticles to stabilize the transient emulsion for a long time.

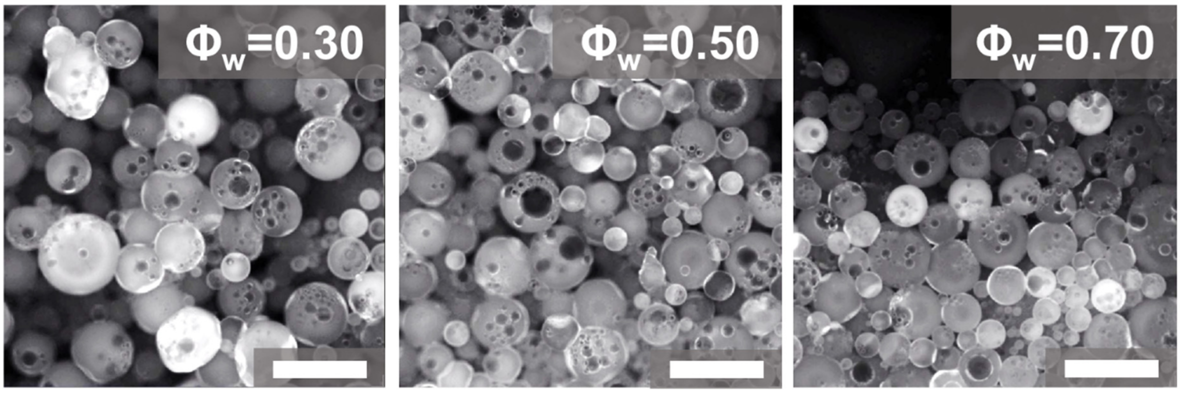

Fig. S7. Fluorescent micrographs of W/O/W double emulsions at 2 hours after emulsification. The concentrations of hydrophilic silica (HDK N20) and the water soluble polymer (PEI) dissolved in deionized water were fixed here as 0.0025 g/mL and 1.0 wt%, respectively. In the micrograph, the bright part corresponds to a soybean oil phase containing an oil-soluble dye (Nile red) while the dark part indicates a water phase. Scale bars, 200µm.

References

1 J. D. Berry, M. J. Neeson, R. R. Dagastine, D. Y. C. Chan and R. F. Tabor, *J. Colloid Interface Sci.* 2015, **454**, 226.

2 J. Saien and S. Akbari, *J. Chem. Eng. Data* 2006, **51**, 1832.