Preparation of oil-containing polymeric particles having a single depression with various shapes

Electronic Supplementary Information

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Fig. S1 OM images of silicone oil droplets observed before (A) and after (B, C, D and E) the addition of MPTMS to PDMS emulsion. MPTMS/DMDES volume ratios were 0.13 (B), 0.24 (C), 0.40 (D) and 1.0 (E). All scale bars represent 5 μm.



Fig. S2 Size distribution of polymerized particles (Fig. 2 (C)) formed at the MPTMS/DMDES ratio of 0.40. The size distribution was measured at 30 min after the addition of MPTMS.



Fig. S3 SEM images of the particles obtained in copolymerization with MPTMS and St at different MPTMS/DMDES ratios of 0.13 (A,A'), 0.24 (B,B') and 0.40 (C,C'). The images of (A–C) were pictured for particles as prepared and the ones of (A' –C') for particles after centrifugation. The concentrations of St and KPS were fixed at 16.8 mM and 1 mM, respectively. All scale bars represent 2 μ m.



Fig. S4 TGA profiles (A) obtained by analyzing the particle presented in Fig. 5. Red, green and blue curves show the profiles of the particles prepared at MPTMS/DMDES volume ratios of 0.13, 0.24 and 0.40. TEM images (B) and elemental mappings (C) were pictured for the particles synthesized at the MPTMS/DMDES ratio 0.13 (1) and 0.40 (2). Scale bars in the TEM image represent 2 μ m. Red and green dots in the elemental mapping image indicate carbon and silicon, respectively.

S5 Estimating volume shrinkage of an oil phase during polymerization

The shrinkage volume ratio ΔV described in the text is defined as follows:

$$\Delta V = V_{shrink} / V_{droplet} \tag{1}$$

where V_{droplet} is the volume of oil droplet before polymerization, $V_{\text{shrinkage}}$ the volume of shrinkage during the polymerization volume (also See Fig. S5.1).



Fig. S5.1 Definition of V_{shrink} and $V_{droplet}$.

5-1 Volume shrinkage of an oil phase during polymerization without St addition

5-1-1 Shrinkage volume estimated by density difference between reactants and products during the polymerization. In the polymerization to form polymeric shell, MPTMS incorporated into the oil droplet was reacted with each other and densified from 1.045 g/cm³ to 1.228 g/cm³ according to the report by Sacanna et al.^{S1}. At the volume ratio of MPTMS/DMDES = 0.40, the oil-contained particles with a depression volume of $\Delta V = 0.043$ was estimated by the polymerization.

5-1-2 Shrinkage volume measured with the particle dimension in SEM image.

Under an assumption that total shell surface area does not change during shell deformation in the polymerization (See Fig. S5.2), the shrinkage volume ratio ΔV is calculated from the following equation (2):

$$\Delta V = 1 - \frac{3}{4} \left(\frac{3}{2} \sin \theta + \frac{1}{6} \sin 3\theta \right)$$
 (2)

where $\theta = \cos^{-1}(r/R)$, *r* the radius of a circular dimple, *R* the radius of a particle. At MPTMS/DMDES = 0.40 where polymeric particles with $r = 0.62 \ \mu m$ and $R = 1.06 \ \mu m$ were formed, the shrinkage volume ratio ΔV was calculated to $\Delta V = 0.048$.



Fig. S5.2 Indication of *r* and *R*.

5-2 Volume shrinkage of an oil phase during polymerization with St addition

5-2-1 Shrinkage volume estimated by density differences between reactants and products during the polymerization. Similarly to the section 4-1-1, the shrinkage volume of an oil phase was estimated for the polymerizations at the ratios of MPTMS/DMSES = 0.40 and St/DMDES = 0.19. Using 0.906 g/cm³ and 1.05 g/cm³ as densities of styrene and polystyrene, respectively, the oil-contained particles with a depression volume of $\Delta V = 0.043$ was estimated by the polymerization.

5-2-2 Shrinkage volume measured with the particle dimension in SEM image. According to the equation (2) and the particle dimensions of $r = 0.89 \ \mu\text{m}$ and $R = 1.16 \ \mu\text{m}$, ΔV at the rations was calculated to $\Delta V = 0.170$.

[S1] S. Sacanna, W. T. M. Irvine, L. Rossi and D. J. Pine, Soft Matter, 2011, 7, 1631–1634.



Fig. S6 SEM (A) and OM (B,C) images of the oil-containing particles with the polymeric shells synthesized with MPTMS and St. The images of (A,B) and (C) were pictured at the polymerization times of 20 s and 60 s, respectively. Synthetic conditon: MPTMS/DMDES = 0.13, St/DMDES = 0.19, [KPS] = 1 mM. All scale bars represent 2 μ m.