Supporting Information for:

**CO₂ responsive reversible aggregation of nanoparticles and formation of nanocapsules with an aqueous core**

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Scheme S1. Chemical structures of initiators used in this study: 2,2'-azobis(2-methylbutyronitrile) (V59), 10 h half-life decomposition temperature 67 °C; 2,2'-azobis(4-methoxy-2,4-dimethyl valeronitrile) (V70), 10 h half-life decomposition temperature 30 °C.

Scheme S2. a) The transition amphiphilic (DDAH+HCO₃⁻) to hydrophobic (DDA) occurs during the polymerization and directly decreases the number of surfactants (state II), and as a result the monomer droplets become unstable and are subjected to coalescence and Ostwald ripening (state III) to form large polymer particles (state IV); b) by addition of HD into the system, monomer droplets are more stable towards Ostwald ripening, and therefore no large particles are formed after polymerization (state III).
Figure S1. $^1$H-NMR spectra of DDAH$^+\text{HCO}_3^-$ in D$_2$O (3.0 mg·mL$^{-1}$) measured before sonication, after sonication, and after recharging CO$_2$.

Figure S2. $^1$H-NMR spectra of MMA and styrene in DMSO-$d_6$ were taken before (black) and after (red) polymerization, and pyrene (8.0–8.5 ppm) was used as an external label to calculate the monomer conversions: a) integrals of protons at ~6.09 ppm and ~5.55 ppm in MMA significantly decreased after polymerization; b) integrals of protons at ~6.70 ppm, 5.84 ppm and ~5.26 ppm in St decreased after polymerization. The resonance peaks of aromatic protons in PS could not be detected. This is due to the poor solubility of PS in DMSO-$d_6$ (0.55 mL) and D$_2$O (50 μL) mixed solvent. We also observed the turbidity of the PS samples during the $^1$H-NMR measurements.

Figure S3. SEM micrographs of PMMA particles obtained by miniemulsion polymerization at 60 °C, using DDAH-HCO$_3$ as surfactant and V70 as initiator: a) and b) are samples prepared without HD (Table 1 Entry 5); c) and d) are samples prepared with HD (Table 1 Entry 6).
Figure S4. SEM micrographs of PS particles obtained by miniemulsion polymerization at 80 °C, using DDAH`HCO₃⁻ as surfactant and V59 as initiator: a) and b) are samples prepared without HD (Table 1 Entry 3); c) and d) are samples prepared with HD (Table 1 Entry 4).
Figure S5. SEM micrographs of PS particles obtained by miniemulsion polymerization at 60 °C, using DDAH\(^{-}\)HCO\(_3\)\(^{-}\) as surfactant and V70 as initiator: a) and b) are samples prepared without HD (Table 1 Entry 7); c) and d) are samples prepared with HD (Table 1 Entry 8).
Figure S6. SEM and TEM micrographs for PVF capsules with thin shell: a) and b) with DDA as the liquid core; c) and d) with water as the liquid core. PVF capsules were prepared by using PVF and DDA (1:1 by weight).