Electronic Supplementary Material (ESI) for Polymer Chemistry
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Electronic Supplementary Information

Capsule clusters fabricated by polymerization based on capsule-in-water-in-oil Pickering emulsions

Yu Yang, Yin Ning, Chaoyang Wang* and Zhen Tong

The number of the small capsule in a capsule cluster and the volume percentage of the voids in a capsule clusters

In a capsule-in-capsule, the number of the small capsules in a big capsule can be calculated approximately by the following equation:

$$N=AD^3/d^3$$

N presents the number of the small capsules in a big capsule; A stands for the concentration of the PU capsule in the aqueous dispersion. D stands for the diameter of the capsule clusters; d presents the diameter of the inner capsules. For example, the number of C5 in CC2 capsule clusters can be calculated to be ca. 1600.

As the C/W/O droplet size had little change after the capsule polymerization, the volume percentage of the voids in a capsule structure could be calculated approximately as the equation: $\theta= 1-A-B$, B stands for the concentration of pre-MF monomers. For example, the volume percentage of the voids in CC2 capsule clusters can be calculated to be 50 %.

The DBP loading effiencies of PU capsules and the capsule clusters

The loading efficiencies of DBP were determined by acetone extraction as follows: Firstly, a Pickering emulsion which was containing W_0 g of DBP was used to fabricate DBP-loaded microcapsules as the above process. All of the obtained

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microcapsules were weighted as W_1 g, and then the microcapsules were ground with a pestle in a mortar at room temperature. After enough grind, acetone was added into the mortar to wash the leaked DBP. This mixture suspension was centrifuged at 12000 rpm for 3 min, and then the DBP acetone supernatant was decanted from the tubes. This process was repeated for three times. The sediment was dried in a vacuum oven at 70 °C. After cooling in a vacuum desiccator, this sediment was weighed (W_2). Eventually, the loading efficiency of these capsules in the process of encapsulation (η_1) was calculated by:

$$\eta_1=[(W_1-W_2)/W_0]\times100\%$$

For example, the loading efficiency of C5 capsules came to be ca. 94 wt. %.

As the same method, the loading efficiency of DBP in capsule clusters (η_2) was determined. W_3 g of PU capsules was used to fabricate capsule clusters as the above process. All of the obtained capsule clusters were weighted as W_4 g, and then the capsule clusters were ground with a pestle in a mortar at room temperature. After enough grind, acetone was added into the mortar to wash the leaked DBP. This mixture suspension was centrifuged at 12000 rpm for 3 min, and then the DBP acetone supernatant was decanted from the tubes. This process was repeated for three times. The sediment was dried in a vacuum oven at 70 °C. After cooling in a vacuum desiccator, this sediment was weighed (W_5). Eventually, the loading efficiency of these capsule clusters in the process of encapsulation (η_2) was calculated by:

$$H_2=[(W_4-W_5) / (C_M W_3)] \times100\%$$

C_M is the real DBP loading capacity of PU capsules which is determined by TGA.

The DBP loading efficiency of CC2 capsule clusters came to be ca. 87 wt. %.

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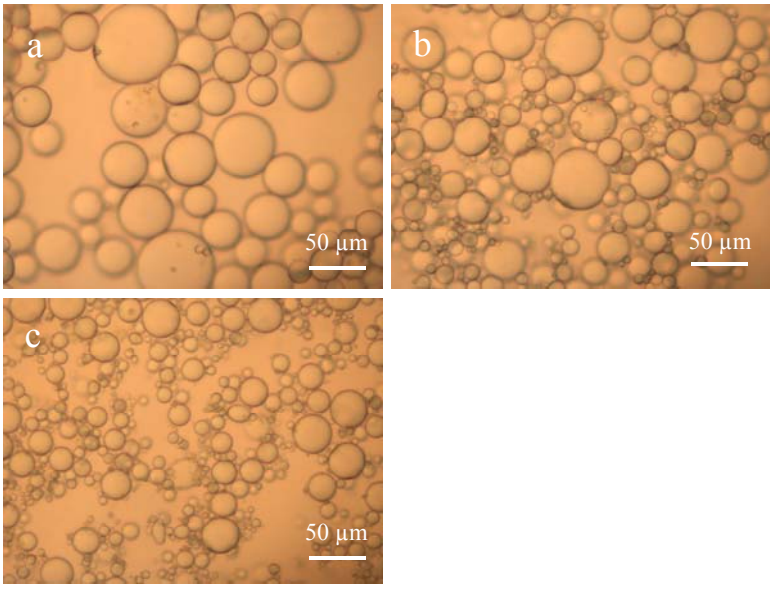

Figure S1. Optical microscopic images of the O/W Pickering emulsions stabilized by N20 nanoparticles with the volume ratios of water to oil: (a) 1:1, (b) 3:1, and (c) 6:1.

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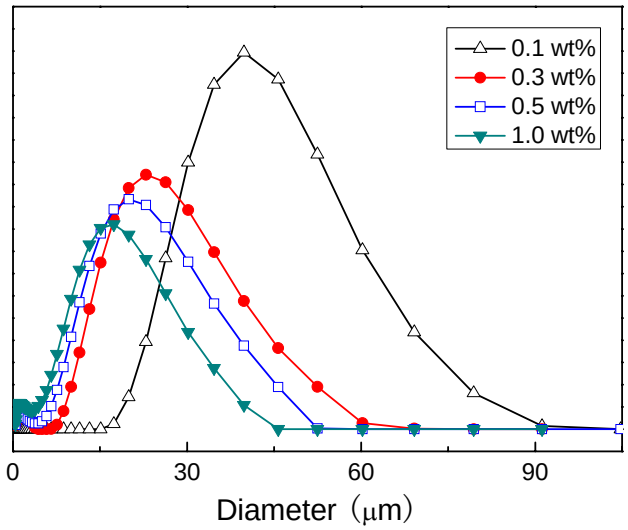

Figure S2. Size distribution graphs of Pickering emulsions with different N20 nanoparticle concentrations.

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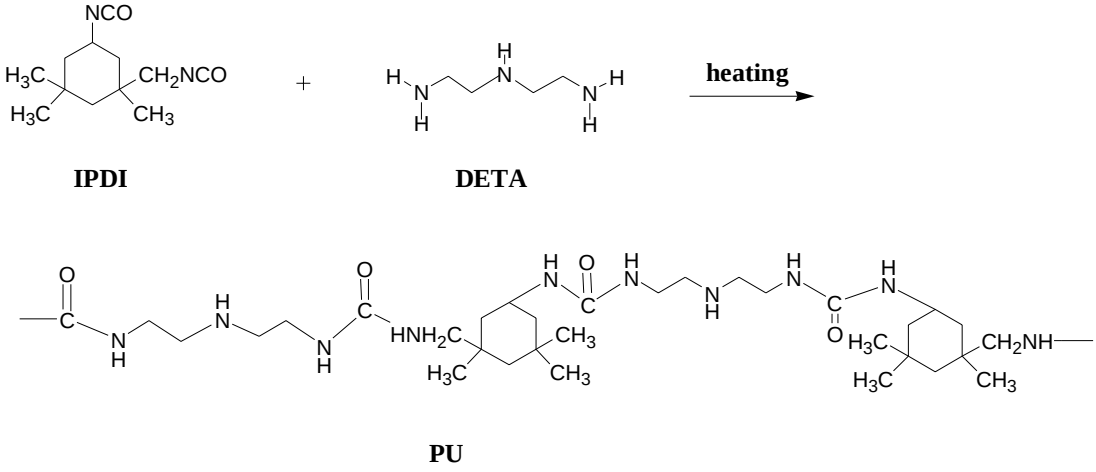

Figure S3. The reaction between IPDI and DETA to form PU.

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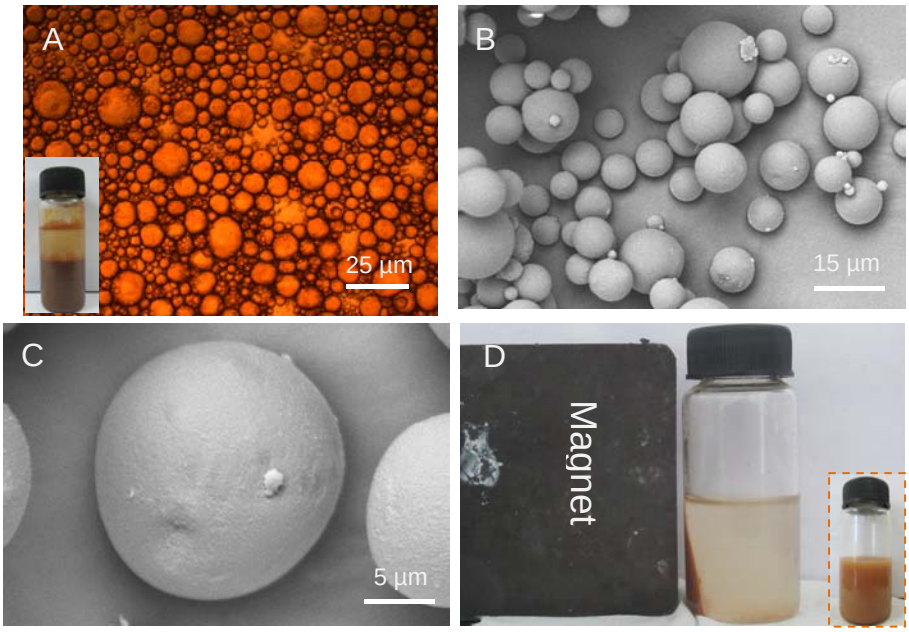

Figure S4. (A) Optical microscopic image of the O/W Pickering emulsions stabilized by Fe_3O_4 nanoparticles. The inset in (A) is the photo of the Fe_3O_4 nanoparticle-stabilized O/W Pickering emulsion. (B) and (C) are SEM images of DBP-loaded PU capsules prepared via the emulsion stabilized by 1.0 wt % Fe_3O_4 nanoparticles in the water phase. (D) Photos of the microcapsules in water under an external magnetic field and the inset in (D) shows microcapsules in water without an external magnetic field.

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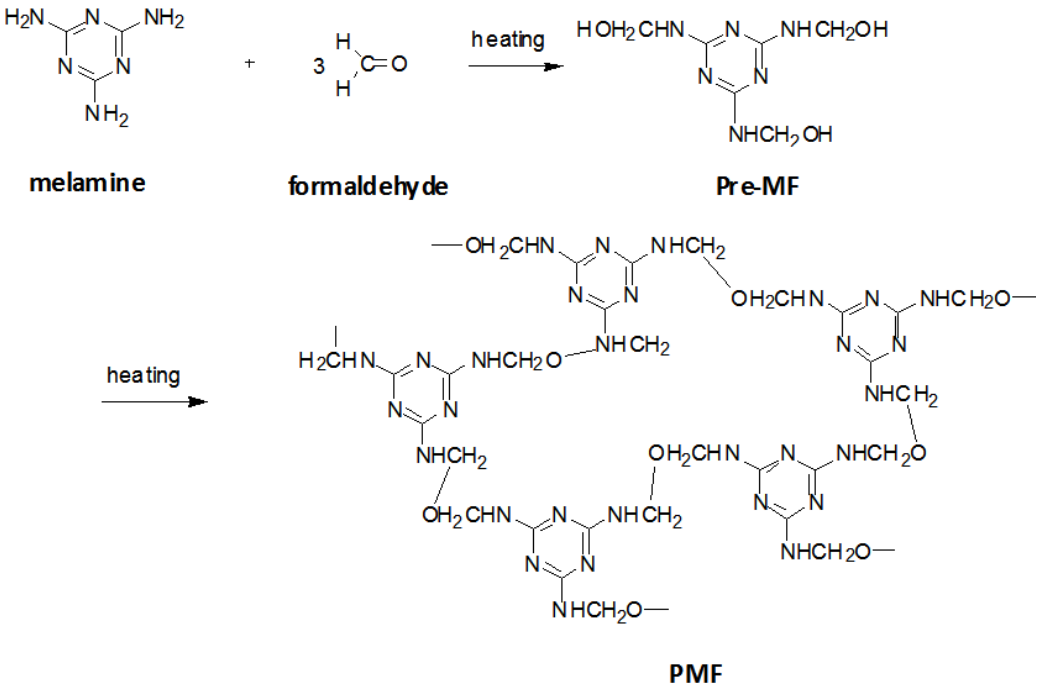

Figure S5. The reaction between melamine and formaldehyde to form pre-MF and PMF.

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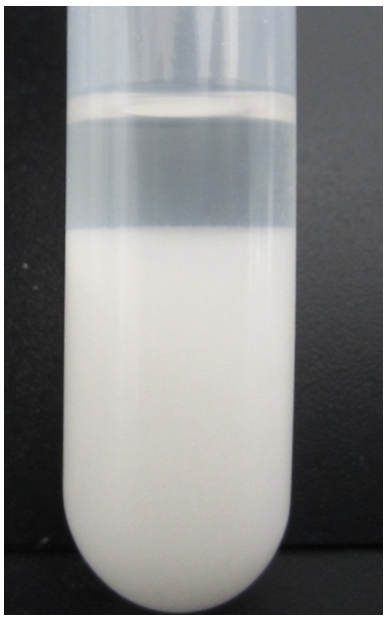

Figure S6. Digital photo of the stable C/W/O emulsion. The volume ratio of oil to water is 3:1.

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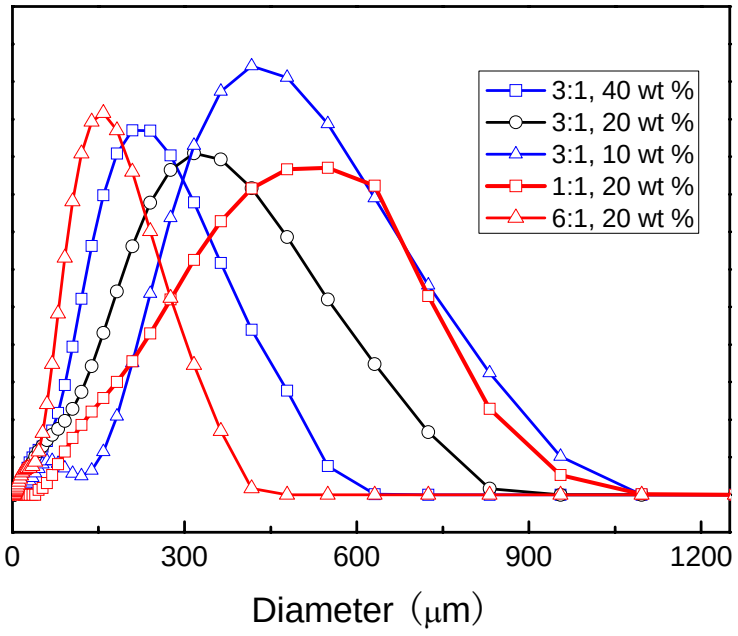

Figure S7. Size distribution graphs of the capsule clusters of CC1, CC2, CC3, CC4 and CC7 in Table 2.

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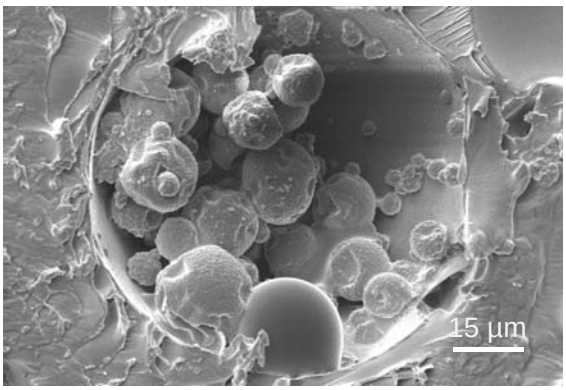

Figure S8. SEM image of the fracture surface of the epoxy resin containing EPA-loaded capsule clusters of 10 wt%.

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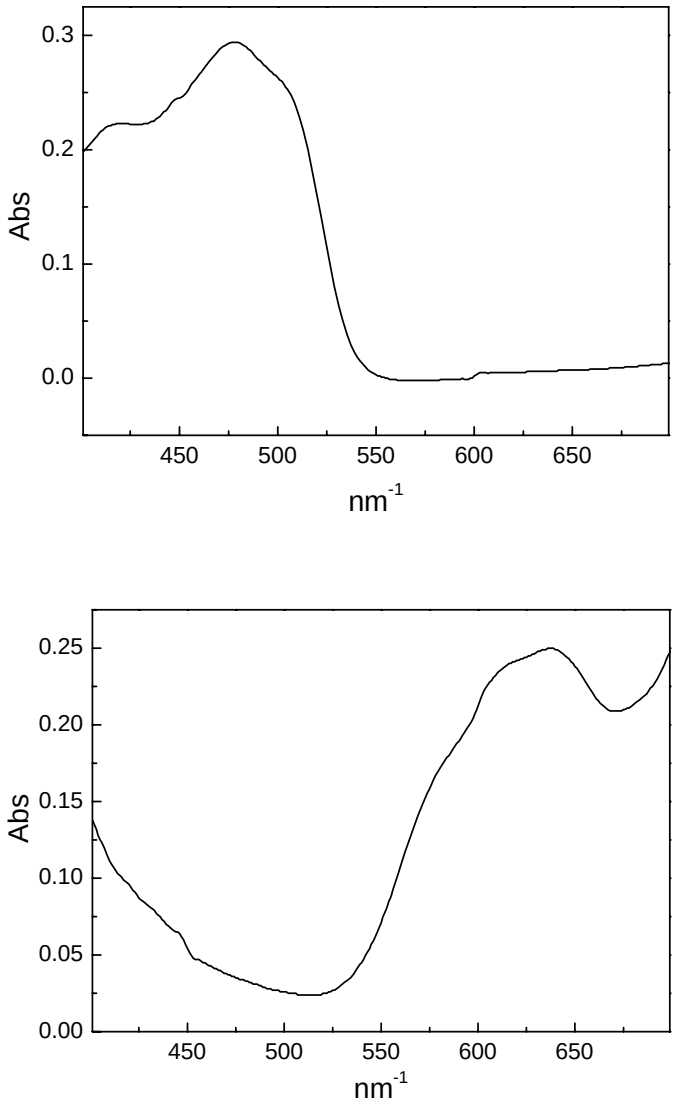

Figure S9. The UV spectra of (a) Sudan I and (b) oil soluble blue in ethanol. The 480 nm^{-1} peak is characteristic peak of Sudan I, and the 640 nm^{-1} peak is characteristic peak of oil soluble blue.