

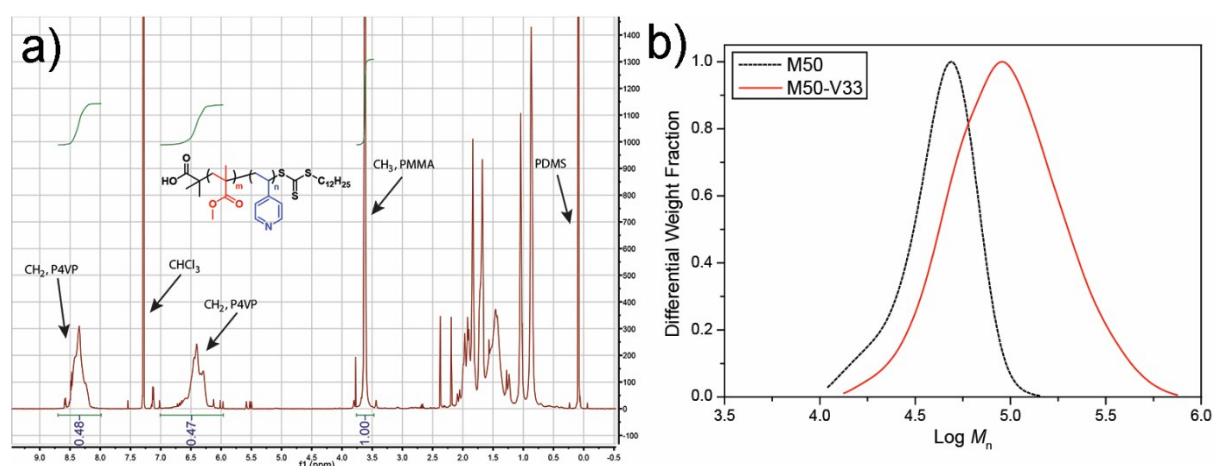
Supporting Information

In situ Crosslinking of Nanostructured Block Copolymer Microparticles in Supercritical Carbon Dioxide

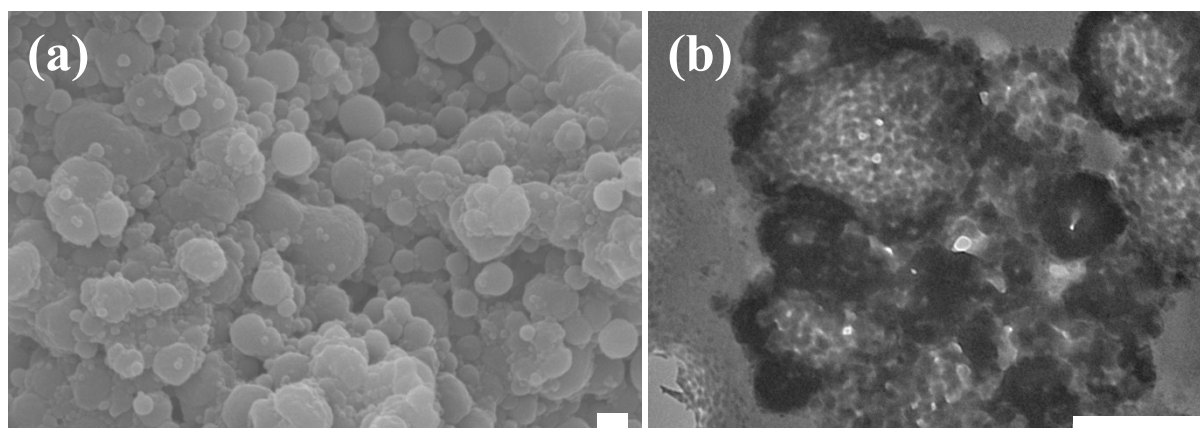
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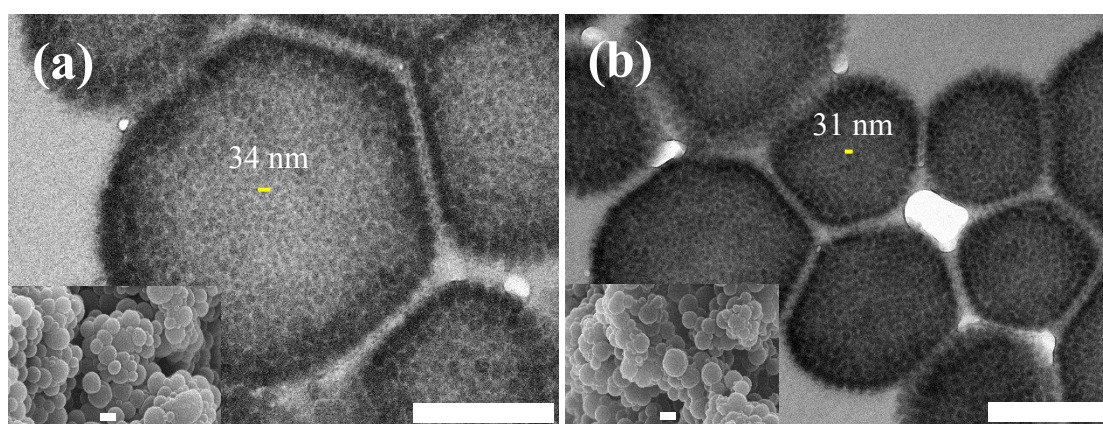
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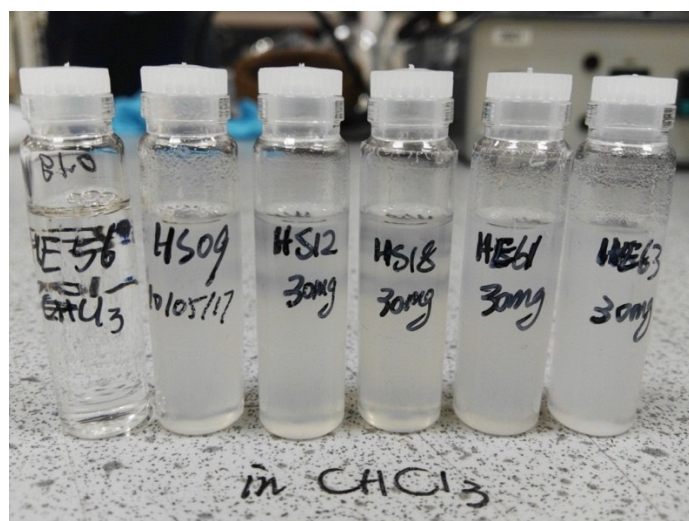
SI Fig. 1. (a) ¹H NMR spectrum of non-crosslinked **M50-V33**, enabling the proportion of P4VP to be calculated. (b) GPC molecular weight distribution data (normalised to peak height) for the PMMA first block (**M50**) and the final block copolymer (**M50-V33**) after chain extension with P4VP.



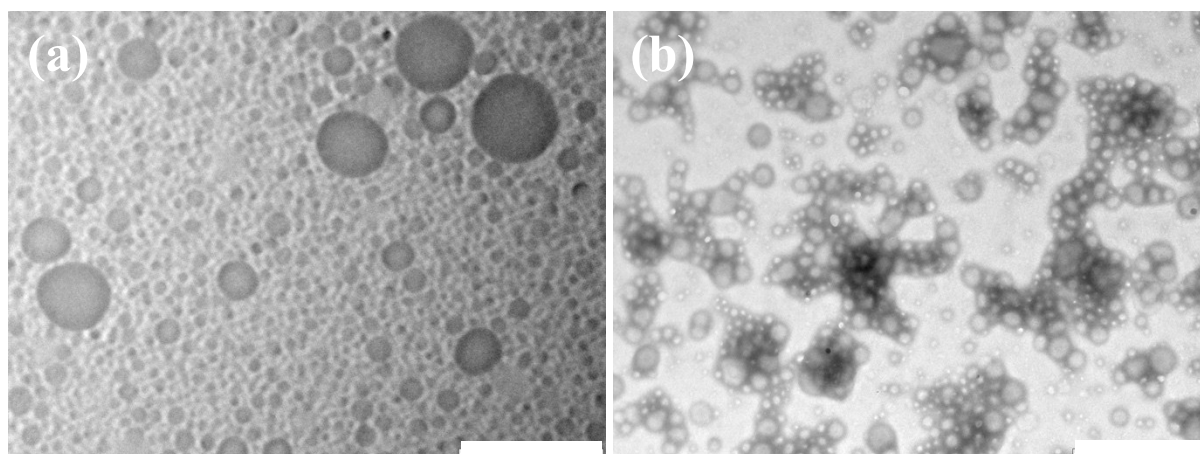
SI Fig. 2. SEM (a) and TEM images (b) of M50-V33/D1. Scale bar represents 500 nm.



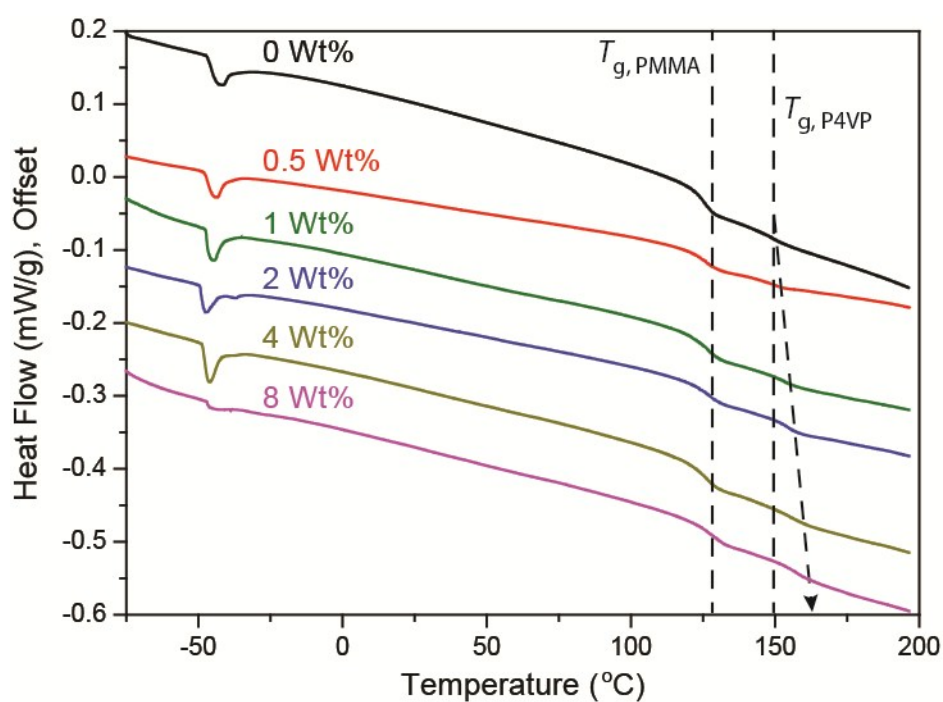
SI Fig. 3. SEM (inserts) and TEM images of (a) M50-V₁₇-V₂₁₆/D2 and (b) M50-V₁₇-V₂₁₆/D4. Scale bar represents 500 nm in the cross-sections and 1 μm in the inserts.



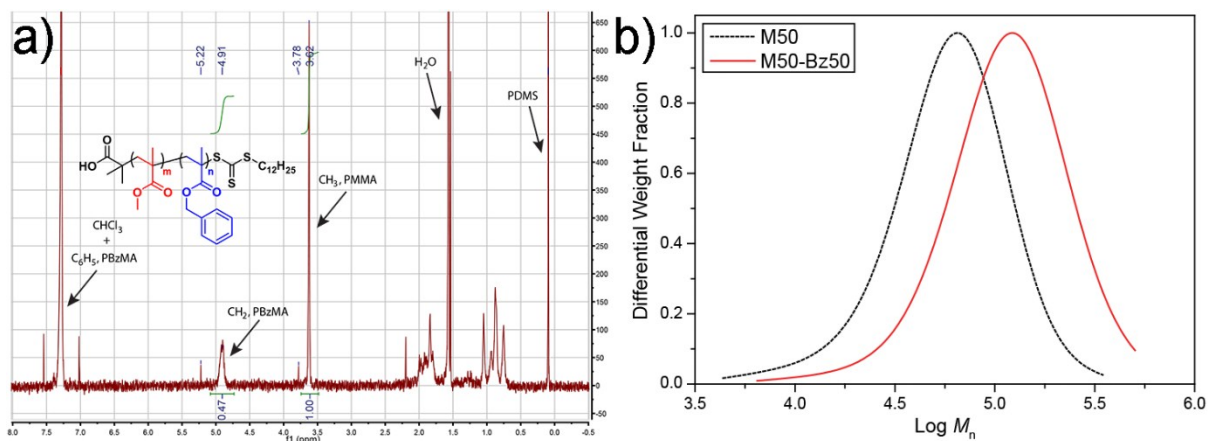
SI Fig. 4. Photographic image of the samples dispersed in chloroform. From left to right: M50-V33, M50-V33/D1, M50-V33/D0.5, M50-V₁₇-V₂₁₆/D1, M200-V₁₈₀-V₂₅₂/D4, M50-V₁₂₀-V₂₁₃/D8.



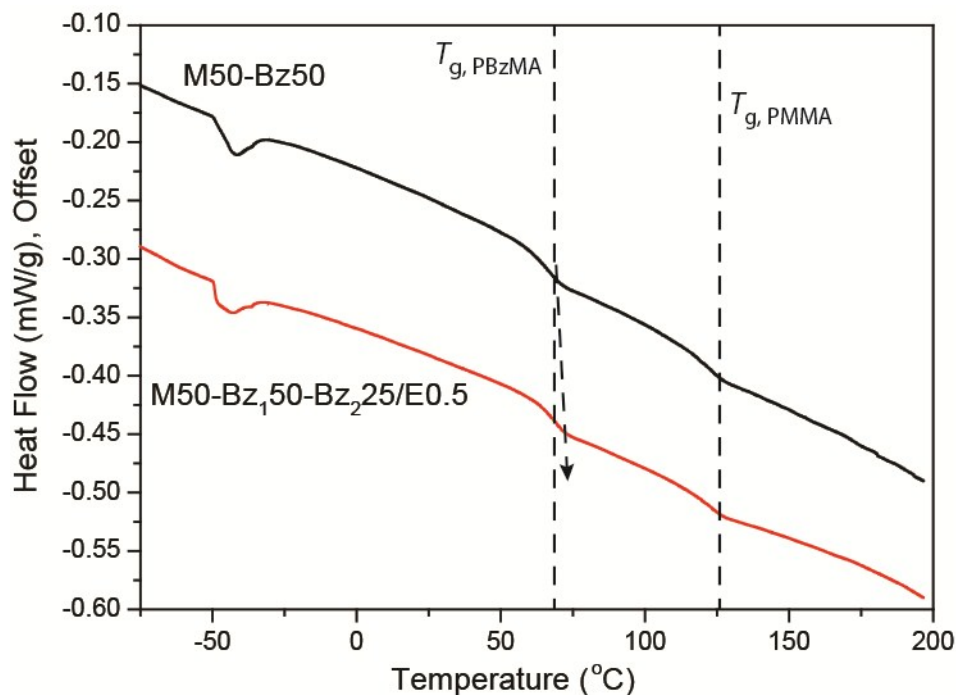
SI Fig. 5. TEM images of **M50-V33** at a concentration of 2 mg/ml in THF. Samples were stained with I_2 vapour for 2 h. The scale bar in both images is 500 nm.



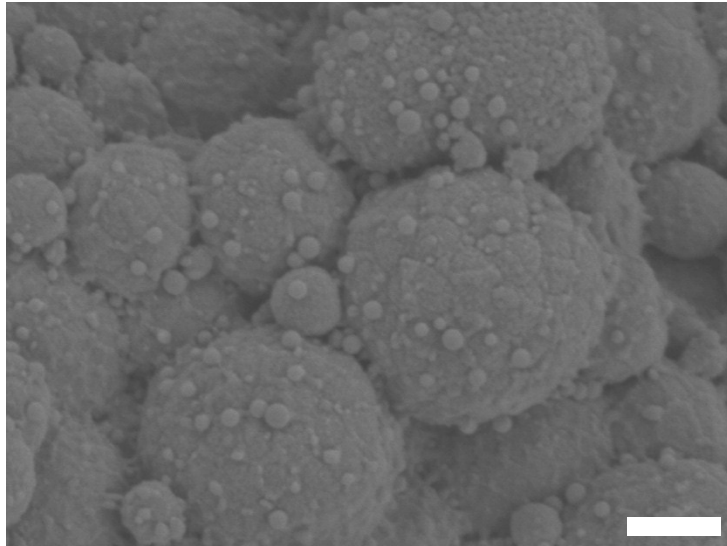
SI Fig. 6. DSC traces for the crosslinked PMMA-*b*-P4VP samples prepared via the two-step method. The lines show the positions of the T_g value of the non-crosslinked PMMA and P4VP BCP sample. The arrows highlights the increasing T_g values of the crosslinked P4VP domains.



SI Fig. 7. (a) ^1H NMR spectrum of non-crosslinked **M50-Bz50**, enabling the proportion of PBzMA to be calculated. (b) GPC molecular weight distribution data (normalised to peak height) for the first PMMA block (**M50**) and the final block copolymer (**M50-Bz50**) after chain extension with BzMA.



SI Fig. 8. DSC traces of **M50-Bz50** (black) and **M50-Bz₁₅₀-Bz₂₅/E0.5** (red).



SI Fig. 9. SEM image of the **M50-V₁20-V₂13/D8** microparticles after swelling in ethanol. The scale bar represents 500 nm.