Supporting Information

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

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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-V_{17-V_{216}/D2} and (b) M50-V_{17-V_{216}/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-V_{33}, M50-V33/D1, M50-V33/D0.5, M50-V_{17-V_{216}/D1}, M200-V_{80-V_{2152}/D4}, M50-V_{120-V_{213}/D8}. 
SI Fig. 5. TEM images of M50-V33 at a concentration of 2 mg/ml in THF. Samples were stained with I₂ 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) $^1$H 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.