Supporting Information

Synthesis of Two-phase Polymer Particles in Supercritical Carbon Dioxide

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Additional Experimental

For analytical comparison, pure PMMA particles and homopolymers of BzA and BA were synthesised by the following methods.

PMMA Particle Synthesis

The same procedure as described in the manuscript was followed, for the initial stage of the reaction with the following amounts were used: MMA (9.0 mL, 83.66 mmol), AIBN (1 wt% with wrt total MMA, 0.09 g, 0.55 mmol) and PDMS-MA (5 wt% wrt total MMA, 0.47 g, 0.047 mmol). In stage two, a charge of MMA (0.89 mL, 8.27 mmol) was added.

PBzA Homopolymer Synthesis

BzA (1 g, 6.17 mmol), AIBN (0.5 wt% wrt BzA, 0.005 g, 0.03 mmol) and toluene (1.3 g, 14.11 mmol) were combined and deoxygenated with argon for 30 minutes. The mixture was heated at 65 °C for 18 hours. The resulting product was precipitated in ice-cold methanol, before being collected by filtration and dried overnight (100 °C).

PBA Homopolymer Synthesis

BA (1 g, 7.80 mmol) and AIBN (0.5 wt% wrt BA, 0.005 g, 0.03 mmol) and toluene (1.3 g, 14.11 mmol) were combined and deoxygenated with argon for 30 minutes. The mixture was heated at 65 °C for 18 hours. The resulting product was precipitated in ice-cold methanol, before being collected by filtration and dried overnight (100 °C).

PMMA Particles Containing PBzA (50 wt%)

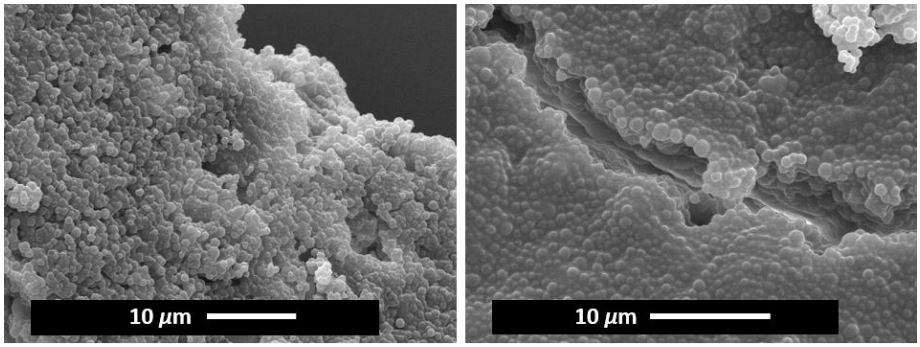

Figure SI-1: *SEM images of particles synthesised using a feed of 50 wt% BzA, added in one step. High levels of agglomeration were observed. Both scale bars are 10 μm.*

PMMA and PBzA UV Analysis

Solutions of PMMA and PBzA (2 mg mL^{-1}) were prepared in THF and the UV spectrum was recorded on a Lambda 25 UV/Vis spectrometer (PerkinElmer). A full wavelength scan (190–900 nm) was performed and data was analysed using UV WinLab (PerkinElmer).

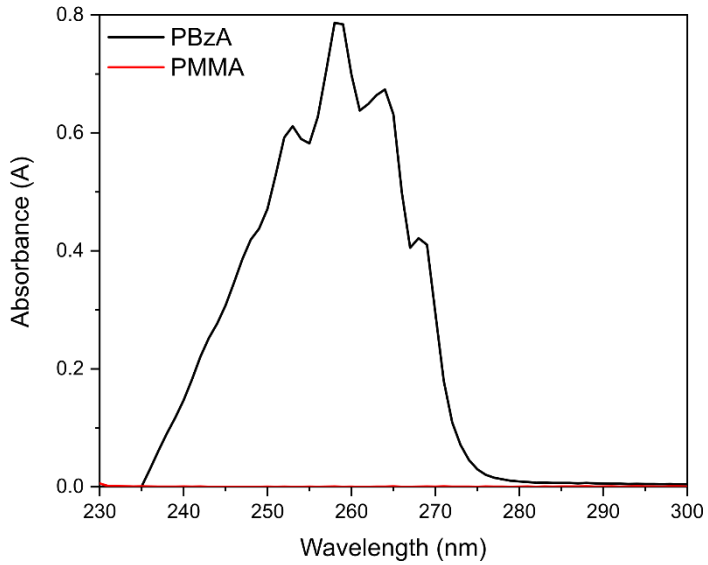

Figure SI-2: *UV analysis performed on PBzA (black trace) and PMMA (red trace). PBzA is UV active in the region between 240-280 nm, typical of aromatic functionalities while PMMA does not show any absorption in the same region.*

PMMA GPC Analysis

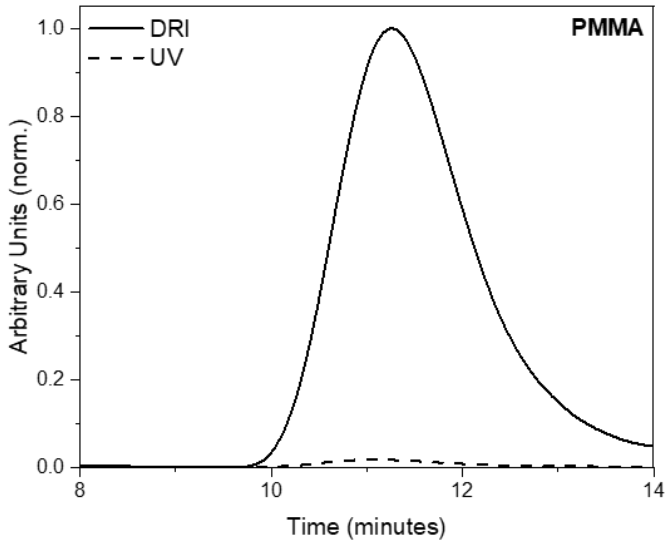

Figure SI-3: *GPC traces obtained for a pure PMMA sample including the DRI (solid line) and UV dashed line) signals. A peak is observed in the DRI signal but not the UV signal.*

PBA and PDMS-MA DMA Analysis

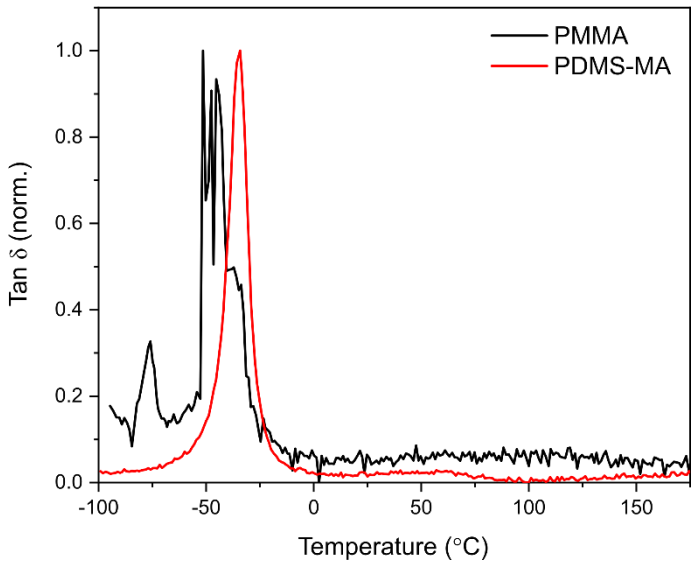

Figure SI-4: *DMA traces showing the overlap of the T_g of PBA and PDMS-MA signals.*

Particles Containing PBA - SEM Analysis

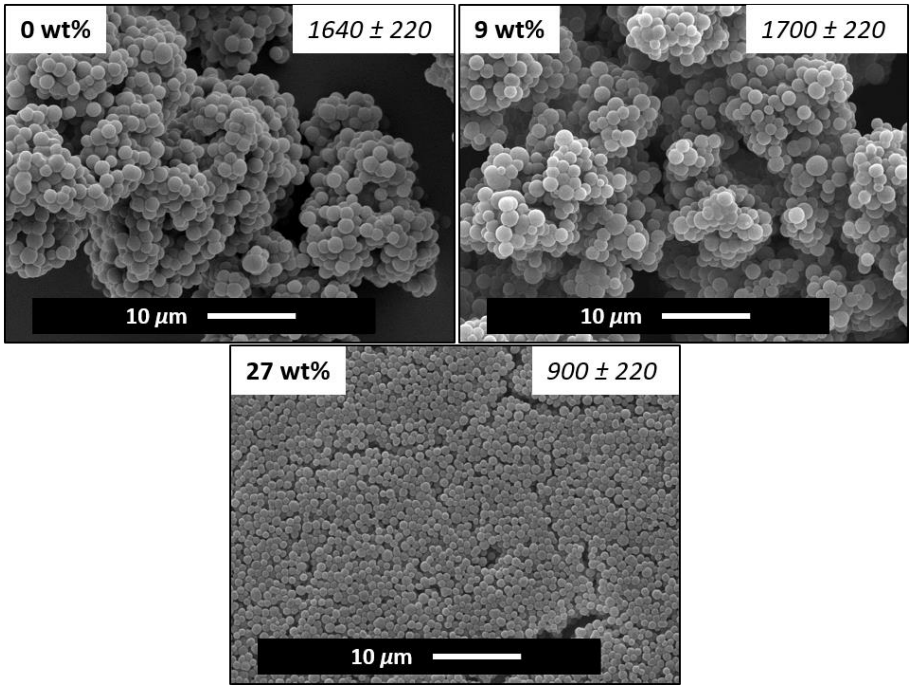

Figure SI-5: SEM images of PMMA particles prepared with different loading of BA, 0, 9 and 27% (as indicated in the top right of each SEM picture). Good spherical particle structure was obtained in each case. All scale bars are 10 µm.