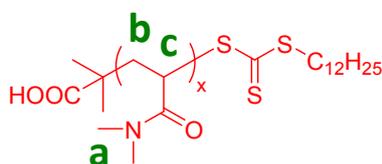


Supporting Information for:

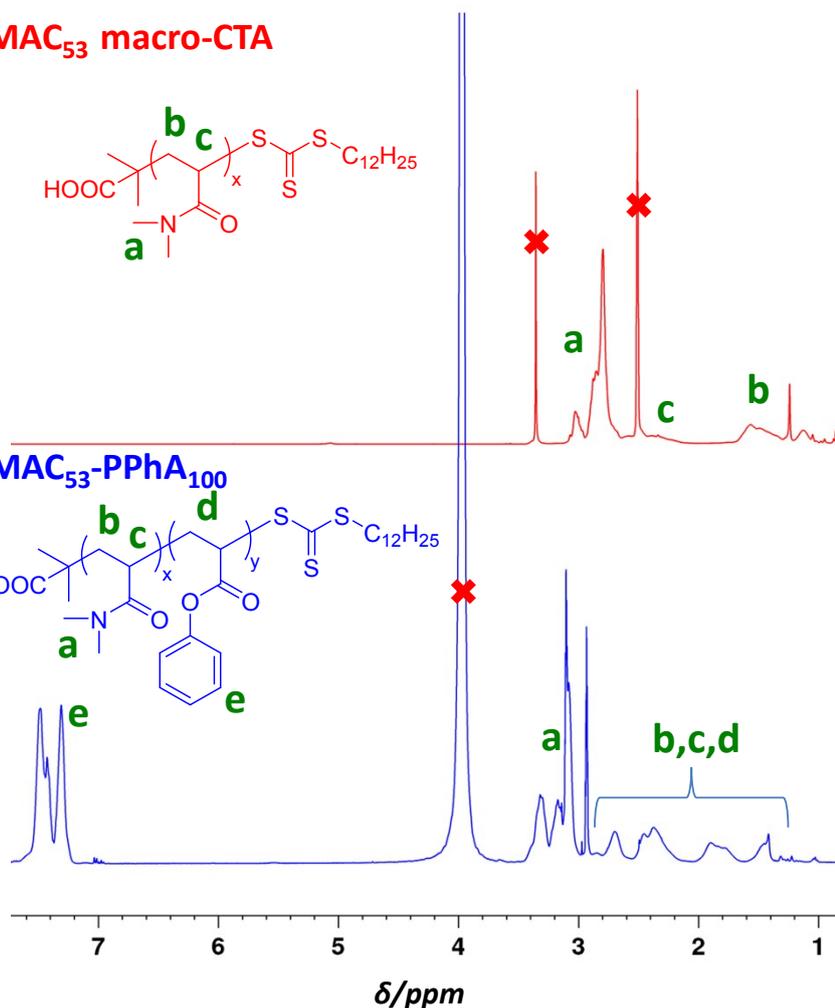
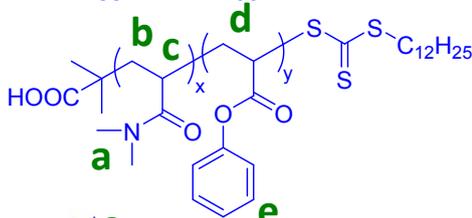
*Phenyl Acrylate is a Versatile Monomer for the Synthesis of Acrylic Diblock Copolymer Nano-objects via Polymerization-Induced Self-Assembly*

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(a) **PDMAC<sub>53</sub> macro-CTA**

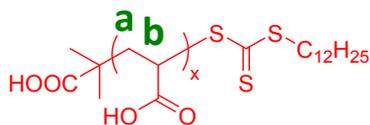


(b) **PDMAC<sub>53</sub>-PPhA<sub>100</sub>**

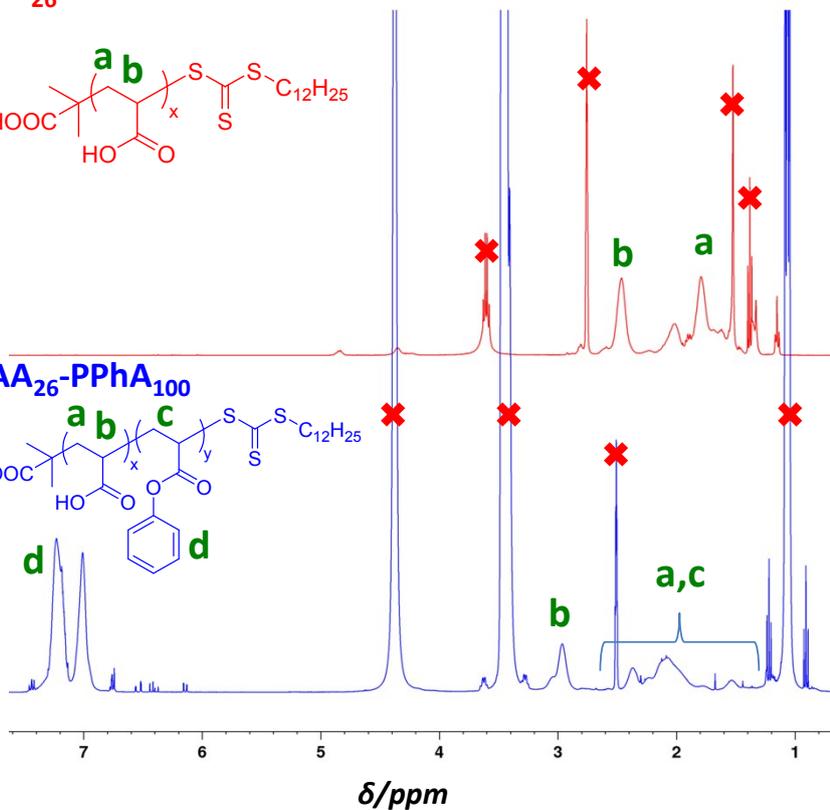
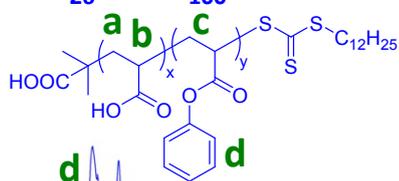


**Figure S1.** <sup>1</sup>H NMR spectra recorded for (a) PDMAC<sub>53</sub> macro-CTA in DMSO-d<sub>6</sub> and (b) PDMAC<sub>53</sub>-PPhA<sub>100</sub> diblock copolymer in DMF-d<sub>7</sub> (>99% PhA conversion after polymerization for 4.5 h in water at 30 °C; DDMAT/initiator molar ratio = 5.0).

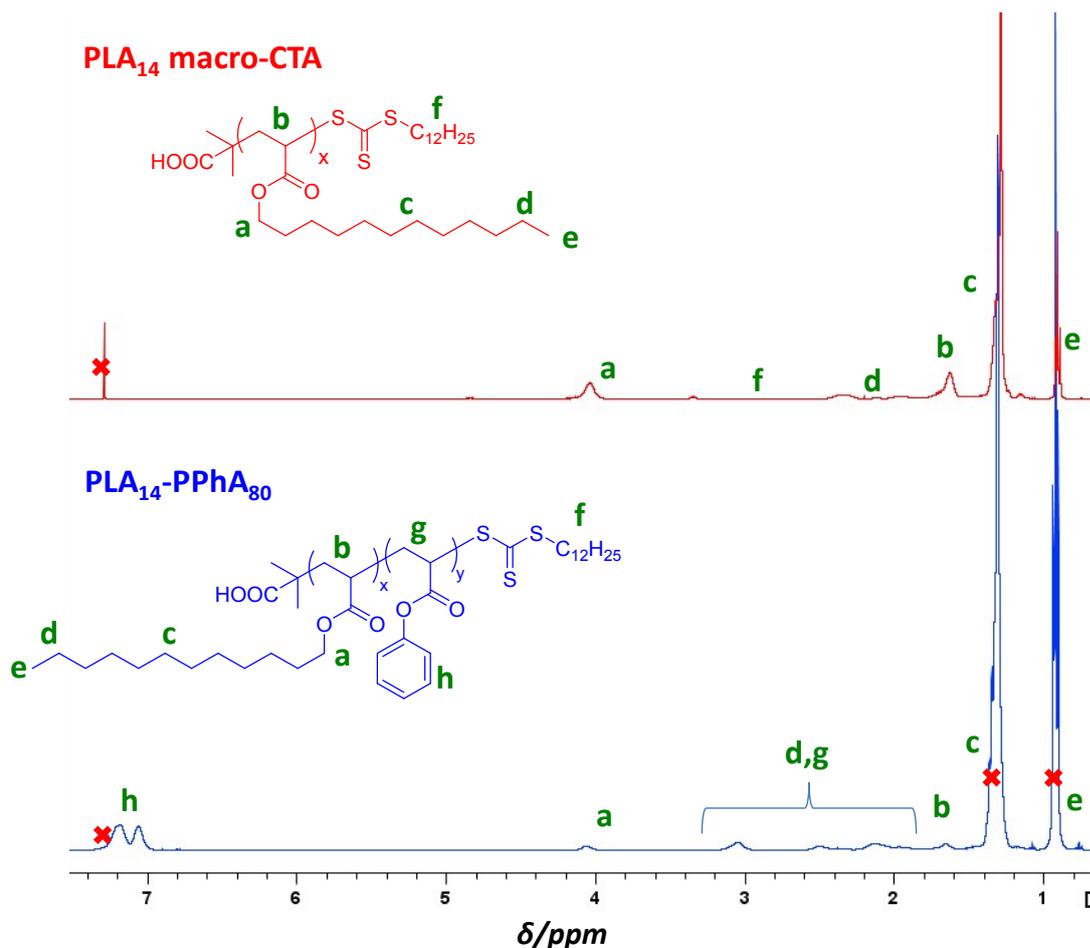
(a) PAA<sub>26</sub> macro-CTA



(b) PAA<sub>26</sub>-PPhA<sub>100</sub>



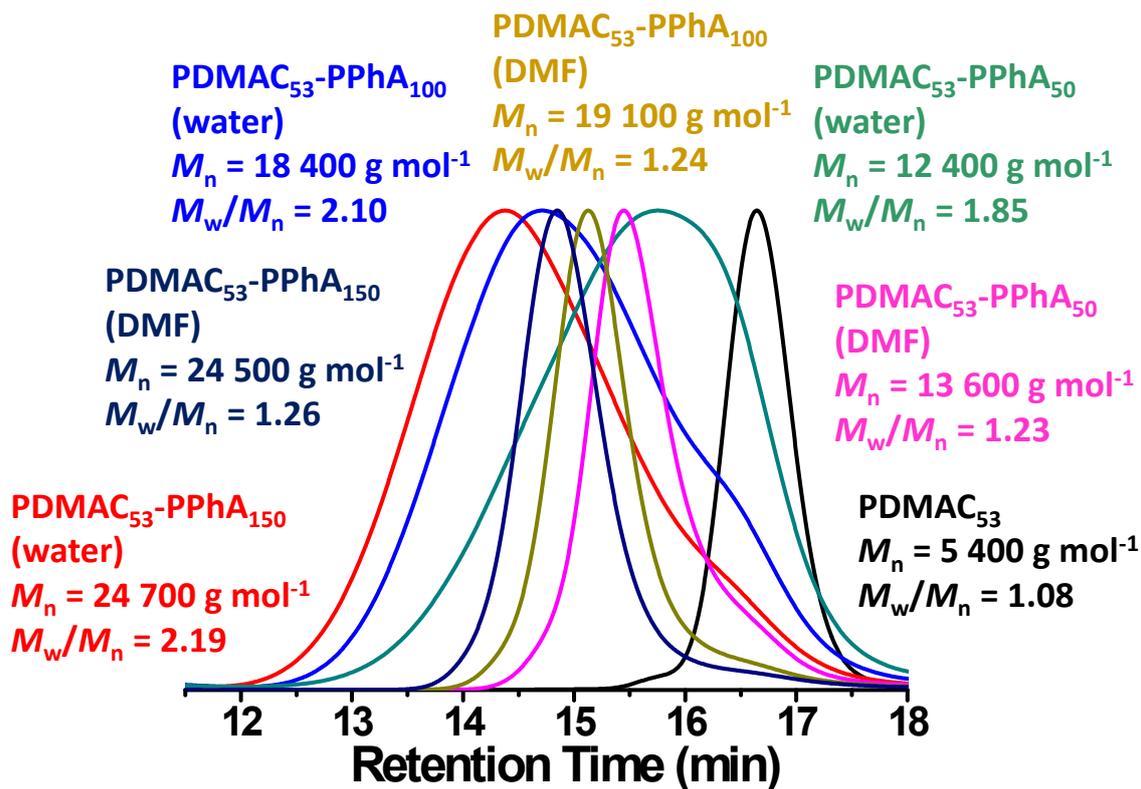
**Figure S2.** <sup>1</sup>H NMR spectra in DMSO-d<sub>6</sub> recorded for (a) PAA<sub>26</sub> macro-CTA and (b) PAA<sub>26</sub>-PPhA<sub>80</sub> diblock copolymer (98% PhA conversion after polymerization in ethanol for 16 h at 70 °C; DDMAT/initiator molar ratio = 5.0).



**Figure S3.** <sup>1</sup>H NMR spectra recorded in CDCl<sub>3</sub> for (a) PLA<sub>14</sub> macro-CTA and (b) PLA<sub>14</sub>-PPhA<sub>100</sub> diblock copolymer (>99% % PhA conversion after polymerization in *n*-heptane for 16 h at 80 °C; CTA/initiator molar ratio = 5.0).

### Synthesis of PDMAC<sub>53</sub>-PPhA<sub>x</sub> Diblock Copolymer Nano-objects by RAFT solution Polymerization in DMF

A typical protocol for the synthesis of PDMAC<sub>53</sub>-PPhA<sub>100</sub> diblock copolymer was as follows: PDMAC<sub>53</sub> macro-CTA (0.24 g, 0.0427 mmol), phenyl acrylate (0.633 g, 4.27 mmol) and DMF (2.6300 g, corresponding to a 25% w/w aqueous solution) were weighed into a 25 mL round-bottom flask, followed by ascorbic acid (1.5 mg, 8.54 μmol), then KPS (2.30 mg, 8.54 μmol; CTA/initiator molar ratio = 5.0). Once dissolved, the solution was degassed with nitrogen for 30 min and then sealed and immersed in an oil bath set at 30 °C. The reaction mixture was stirred for 16 h to ensure high monomer conversion (> 96% by <sup>1</sup>H NMR analysis) and subsequently quenched by cooling to 20 °C, followed by exposure to air. DMF GPC analysis of PDMAC<sub>53</sub>-PPhA<sub>100</sub> indicated  $M_n$  and  $M_w/M_n$  values of 19 100 g mol<sup>-1</sup> and 1.24, respectively.



**Figure S4.** DMF GPC curves for PDMAc<sub>53</sub>-PPhA<sub>x</sub> diblock copolymers prepared at 25% w/w solids and 30 °C via either RAFT aqueous emulsion polymerization or solution polymerization in DMF.  $M_n$  values are expressed relative to a series of near-monodisperse poly(methyl methacrylate) calibration standards. All reactions reached high conversion (>96 %) as judged by <sup>1</sup>H NMR in DMF-d<sub>7</sub>.