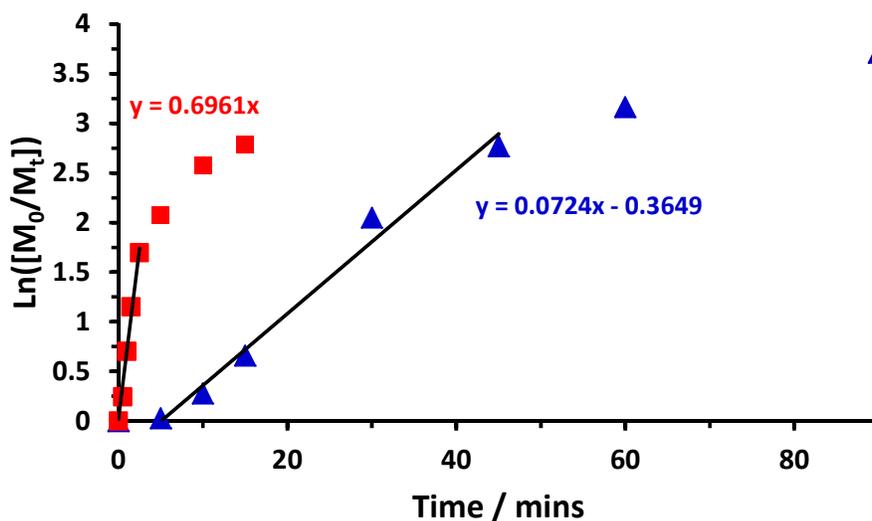


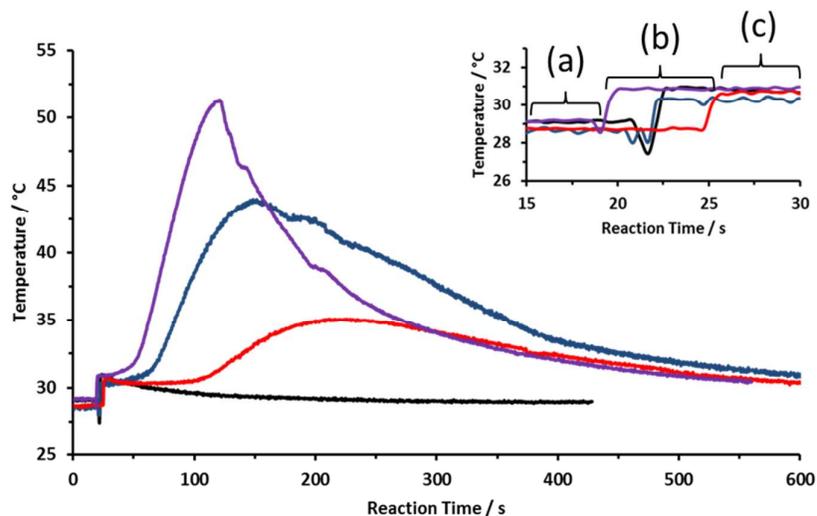
## Supporting Information for:

### Synthesis of Well-defined Pyrrolidone-based Homopolymers and Stimulus-responsive Diblock Copolymers via RAFT Aqueous Solution Polymerization of 2-(N-Acryloyloxy)ethyl Pyrrolidone

*O. J. Deane, J. R. Lovett, O. M. Musa, A. Fernyhough and S. P. Armes\**



**Figure S1.** Semi-logarithmic plots obtained for the RAFT aqueous solution polymerization of NAEP using a DDMAT/initiator molar ratio of 5.0 when using the AIBN initiator (blue triangles) at 70 °C or the KPS/AsAc redox initiator (red squares) at 30 °C (target degree of polymerization = 200 at 60% w/w solids). Equations indicate the gradients associated with each plot, which are proportional to the respective initial rates. Clearly, there is an order of magnitude difference in the initial rate for these two RAFT aqueous solution polymerization formulations.



**Figure S2.** Temperature vs. reaction time plots for the RAFT aqueous homopolymerization of NAEP targeting a DP of 200 using DDMAT/KPS molar ratios of 5.0 (purple), 50.0 (blue) and 100.0 (red). The black data set represents the control experiment where the two reaction solutions were added in the absence of any initiator. Inset shows the initial temperature change when the two reaction solutions were combined.

**Table S1.** Molecular Weight ( $M_n$ ) and Dispersity ( $M_w/M_n$ ) Obtained for a PDEA<sub>100</sub> Homopolymer Prepared by RAFT Solution Polymerization of DEA in THF at 70 °C (AIBN) at 60% w/w Solids.<sup>a</sup> Additionally a Summary of Molecular Weights ( $M_n$ ) and Dispersities ( $M_w/M_n$ ), Z-average Diameter, and PDI Obtained for four PDEA<sub>100</sub>-PNAEP<sub>y</sub> Diblock Copolymers Prepared by RAFT Aqueous Solution Polymerization (pH 2) of NAEP at 30 °C (redox) at 30% w/w Solids.<sup>b</sup>

Polymer Composition	GPC		DLS	
	$M_n$ / g mol <sup>-1</sup>	$M_w/M_n$	Z-average Diameter / nm	PDI
PDEA <sub>100</sub> macro-CTA	10 800 <sup>a</sup>	1.24 <sup>a</sup>	--	--
PDEA <sub>100</sub> -PNAEP <sub>50</sub>	19 100 <sup>b</sup>	1.17 <sup>b</sup>	99	0.07
PDEA <sub>100</sub> -PNAEP <sub>60</sub>	22 700 <sup>b</sup>	1.16 <sup>b</sup>	78	0.08
PDEA <sub>100</sub> -PNAEP <sub>75</sub>	27 900 <sup>b</sup>	1.15 <sup>b</sup>	55	0.07
PDEA <sub>100</sub> -PNAEP <sub>100</sub>	39 500 <sup>b</sup>	1.27 <sup>b</sup>	42	0.13

<sup>a</sup> Determined by chloroform (+ 0.25 v/v % TEA) GPC against a series of near-monodisperse PMMA calibration standards using a refractive index detector. <sup>b</sup> Determined by DMF (+ 0.25 v/v % TEA) GPC against a series of near-monodisperse PMMA calibration standards using a refractive index detector.