# Supporting Information for:

## *Tuning the Critical Gelation Temperature of Thermo-responsive Diblock Copolymer Worm Gels*

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### Synthesis of PGMA-PDEGMA diblock copolymers via RAFT aqueous dispersion polymerization

A typical protocol for the synthesis of $PGMA_{59}$-$PDEGMA_{200}$ diblock copolymer via RAFT aqueous dispersion polymerization is as follows. $PGMA_{59}$ macro-CTA (0.30 g) and DEGMA (1.17 g, 6.23 mmol) were weighed into a 25 ml round-bottom flask and purged with $N_2$ for 15 min. ACVA (3.0 mg, 0.011 mmol; CTA/ACVA molar ratio = 3.0) was added to the flask and the mixture was degassed for 5 min. Water (13.21 ml, 10 wt %), was degassed separately for 30 min and added to the mixture, which was stirred until homogeneous and degassed for a further 10 min prior to immersion in an oil bath at 70 °C for 16 h. The resulting copolymer was analyzed by DMF GPC ($M_n$ = 66,000 g mol$^{-1}$, $M_w/M_n$ = 1.52 vs. PMMA standards).

**Table S1**. Summary of conversions, molecular weights and polydispersities obtained for a $PGMA_{59}$ macro-CTA precursor and various $PGMA_{59}$-PDEGMA diblock copolymers (where G = PGMA and D = DEGMA).

| Target Diblock Composition | Conversion[a] (%) | $M_n$[b] | $M_w/M_n$[b] |
|---|---|---|---|
| **$G_{59}$ macro-CTA** | - | 16,000 | 1.18 |
| **$G_{59}$-$D_{100}$** | >99 | 36,400 | 1.22 |
| **$G_{59}$-$D_{120}$** | 98 | 42,200 | 1.24 |
| **$G_{59}$-$D_{140}$** | 97 | 47,000 | 1.33 |
| **$G_{59}$-$D_{160}$** | 98 | 52,300 | 1.40 |
| **$G_{59}$-$D_{180}$** | >99 | 59,000 | 1.47 |
| **$G_{59}$-$D_{200}$** | >99 | 66,000 | 1.52 |
| **$G_{59}$-$D_{220}$** | >99 | 70,300 | 1.98 |
| **$G_{59}$-$D_{300}$** | >99 | 110,000 | 3.68 |
| **$G_{59}$-$D_{400}$** | 98 | 154,100 | 31.79 |
| **$G_{59}$-$D_{400}$[c]** | >99 | 74,200 | 1.13 |

a. Monomer conversion determined by $^1$H NMR spectroscopy
b. Determined by GPC using DMF eluent and a series of near-monodisperse poly(methyl methacrylates) as calibration standards
c. After purification of DEGMA monomer using silica column chromatography (see also Figure S1 below).

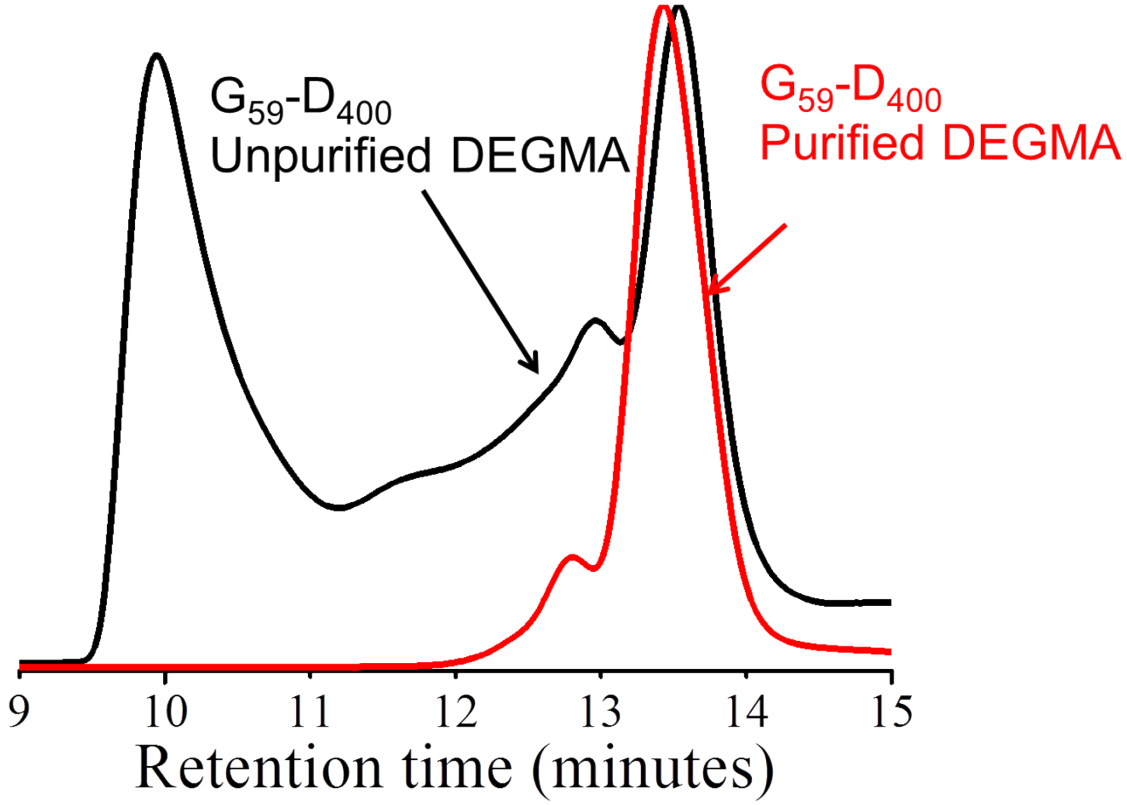


**Figure S1**. DMF GPC curves obtained for $PGMA_{59}$-$PDEGMA_{400}$ diblock copolymers synthesised using either unpurified DEGMA monomer (Aldrich, 95%) or DEGMA purified by silica column chromatography (where G = PGMA and D = PDEGMA).