Supporting Information for:

RAFT dispersion polymerization of benzyl methacrylate in non-polar media using hydrogenated polybutadiene as a steric stabilizer block

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Summary of the additional synthesis details and characterization data

Additional experimental details for the PISA formulations used in this study

Synthesis of PhBD-PBzMA worms by RAFT dispersion polymerization of BzMA

A typical synthesis of PhBD-PBzMA$_{40}$ worms at 40% w/w in *n*-dodecane was conducted as follows: PhBD RAFT agent (0.30 g, 62.0 µmol), BzMA (0.42 g, 2.39 mmol, target DP = 40 assuming a mean degree of esterification of 96% for this PhBD precursor) and *n*-dodecane (1.08 g) were weighed into a 10 mL glass vial equipped with a magnetic stirrer. T21s initiator (2.70 mg, 12.4 µmol, [PhBD]/[T21s] molar ratio = 5.0; 29 µL of a 10% v/v solution in *n*-dodecane) was added to this solution at 20 °C. The resulting mixture was then purged with nitrogen, sealed, and placed in a pre-heated oil bath set at 90 °C for 5 h. After cooling to 25 °C, the final dispersion was obtained as a yellow free-standing gel. ^{1}H NMR spectroscopy studies ($CDCl_3$) confirmed a BzMA conversion of 99 %, and THF GPC indicated an M_n of 14 300 g mol^{-1} and an M_w/M_n of 1.17.

Synthesis of PhBD-PBzMA spheres by RAFT dispersion polymerization of BzMA

A typical synthesis of PhBD-PBzMA$_{300}$ spheres at 25% w/w in *n*-dodecane was conducted as follows: PhBD RAFT agent (0.10 g, 23.1 µmol), BzMA (1.15 g, 6.50 mmol, target DP = 300 assuming a mean degree of esterification of 95% for this PhBD precursor) and *n*-dodecane (3.74 g) were weighed into a 10 mL glass vial equipped with a magnetic stirrer. T21s initiator (1.0 mg, 4.63 µmol, [PhBD]/[T21s] molar ratio = 5.0; 11 µL of a 10% v/v solution in *n*-dodecane) was added to this solution at 20 °C. The resulting mixture was then purged with nitrogen, sealed, and placed in a pre-heated oil bath set at 90 °C for 5 h. After cooling to 25 °C, the final dispersion was obtained as a turbid yellow free-flowing dispersion. ^{1}H NMR spectroscopy studies

($CDCl_3$) confirmed a BzMA conversion of 98 %, and THF GPC analysis indicated an M_n of 50 000 g mol^{-1} and an M_w/M_n of 1.23.

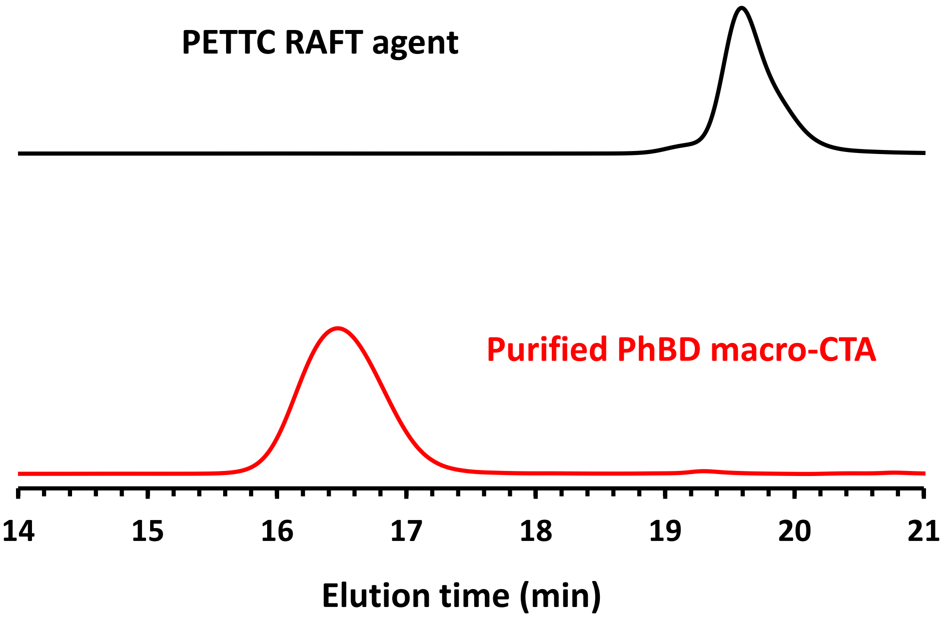
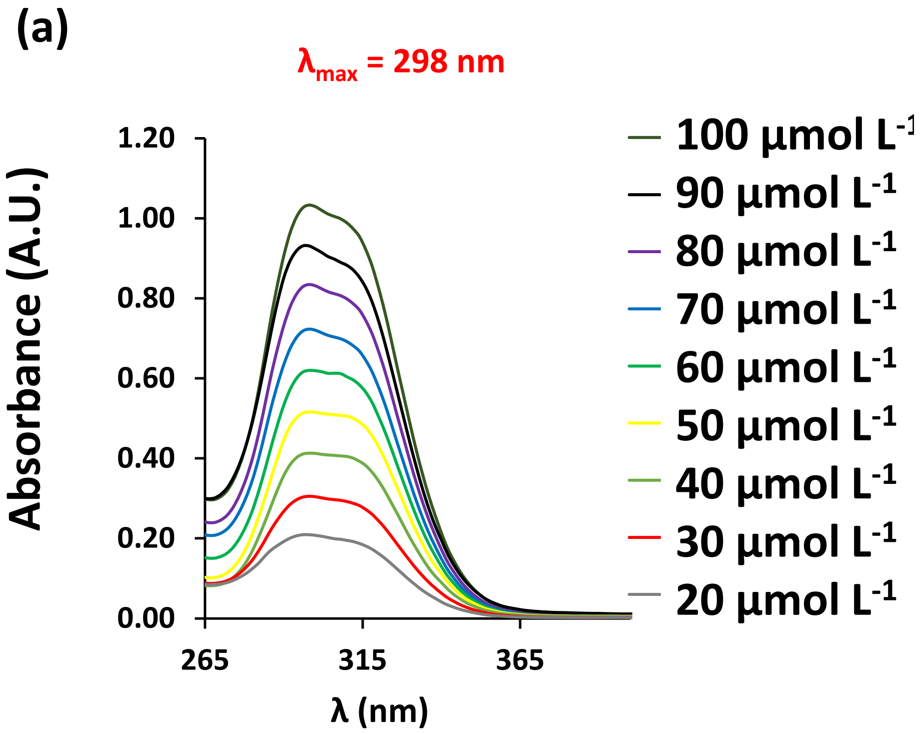


Figure S1. UV GPC curves recorded at λ = 298 nm using THF eluent for PETTC RAFT agent and the purified $PhBD_{80}$ macro-CTA. The absence of any PETTC signal in the $PhBD_{80}$ macro-CTA GPC trace confirms that the purification protocol was successful.



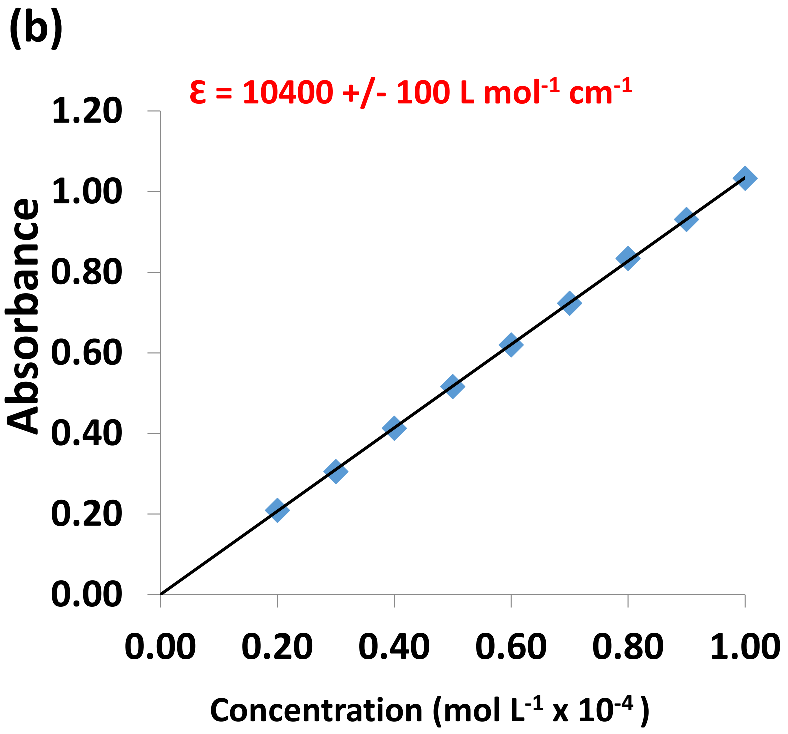


Figure S2. (a) UV spectra recorded for the PETTC RAFT agent dissolved in dichloromethane at various concentrations. (b) Beer-Lambert calibration curve constructed using the absorbance data shown in (a).

Table S1. Summary of characterization data obtained for the diblock copolymers used to construct the phase diagram. BzMA conversions were determined by ^{1}H NMR, molecular weighs were assessed via THF GPC and calibrated against near-monodisperse PMMA standards.

Target Diblock Copolymer Composition	Copolymer concentration %w/w	BzMA conversion %	M_n	M_w/M_n	Copolymer morphology assigned by TEM
PhBD$_{80}$-PBzMA$_{40}$	45	98	14 600	1.10	Worms
PhBD$_{80}$-PBzMA$_{50}$	45	99	17 000	1.10	Worms
PhBD$_{80}$-PBzMA$_{60}$	45	99	18 000	1.13	Mixed
PhBD$_{80}$-PBzMA$_{70}$	45	97	19 100	1.13	Mixed
PhBD$_{80}$-PBzMA$_{80}$	45	99	19 900	1.20	Mixed
PhBD$_{80}$-PBzMA$_{100}$	45	99	24 700	1.13	Mixed
PhBD$_{80}$-PBzMA$_{150}$	45	98	33 000	1.15	Mixed
PhBD$_{80}$-PBzMA$_{200}$	45	98	39 600	1.22	Vesicles
PhBD$_{80}$-PBzMA$_{250}$	45	98	42 300	1.18	Vesicles
PhBD$_{80}$-PBzMA$_{300}$	45	98	52 800	1.21	Vesicles
PhBD$_{80}$-PBzMA$_{40}$	40	97	14 300	1.10	Worms
PhBD$_{80}$-PBzMA$_{50}$	40	98	17 100	1.11	Worms
PhBD$_{80}$-PBzMA$_{60}$	40	98	18 100	1.13	Mixed
PhBD$_{80}$-PBzMA$_{70}$	40	98	19 200	1.13	Mixed
PhBD$_{80}$-PBzMA$_{80}$	40	96	20 200	1.16	Mixed
PhBD$_{80}$-PBzMA$_{150}$	40	98	30 400	1.16	Mixed
PhBD$_{80}$-PBzMA$_{200}$	40	99	37 500	1.19	Mixed
PhBD$_{80}$-PBzMA$_{250}$	40	98	43 300	1.19	Vesicles
PhBD$_{80}$-PBzMA$_{300}$	40	98	49 600	1.20	Vesicles
PhBD$_{80}$-PBzMA$_{30}$	35	97	13 900	1.10	Mixed
PhBD$_{80}$-PBzMA$_{40}$	35	98	14 700	1.10	Mixed
PhBD$_{80}$-PBzMA$_{50}$	35	98	17 200	1.10	Mixed
PhBD$_{80}$-PBzMA$_{60}$	35	98	18 700	1.13	Mixed
PhBD$_{80}$-PBzMA$_{70}$	35	97	19 600	1.14	Mixed
PhBD$_{80}$-PBzMA$_{100}$	35	98	24 300	1.12	Mixed
PhBD$_{80}$-PBzMA$_{150}$	35	98	30 700	1.15	Mixed
PhBD$_{80}$-PBzMA$_{200}$	35	98	38 200	1.17	Mixed
PhBD$_{80}$-PBzMA$_{250}$	35	98	45 500	1.19	Mixed
PhBD$_{80}$-PBzMA$_{300}$	35	98	56 100	1.25	Vesicles
PhBD$_{80}$-PBzMA$_{30}$	30	96	13 700	1.10	Spheres
PhBD$_{80}$-PBzMA$_{50}$	30	97	17 200	1.10	Spheres
PhBD$_{80}$-PBzMA$_{100}$	30	98	23 900	1.13	Spheres
PhBD$_{80}$-PBzMA$_{150}$	30	98	30 800	1.15	Mixed
PhBD$_{80}$-PBzMA$_{200}$	30	98	37 600	1.17	Mixed
PhBD$_{80}$-PBzMA$_{250}$	30	98	45 900	1.20	Mixed
PhBD$_{80}$-PBzMA$_{300}$	30	98	50 000	1.22	Mixed
PhBD$_{80}$-PBzMA$_{30}$	25	98	13 400	1.10	Spheres
PhBD$_{80}$-PBzMA$_{50}$	25	97	17 400	1.11	Spheres
PhBD$_{80}$-PBzMA$_{100}$	25	97	24 700	1.12	Spheres
PhBD$_{80}$-PBzMA$_{150}$	25	98	32 200	1.15	Spheres
PhBD$_{80}$-PBzMA$_{200}$	25	98	44 700	1.21	Spheres
PhBD$_{80}$-PBzMA$_{250}$	25	98	45 000	1.20	Spheres
PhBD$_{80}$-PBzMA$_{300}$	25	98	50 100	1.23	Spheres

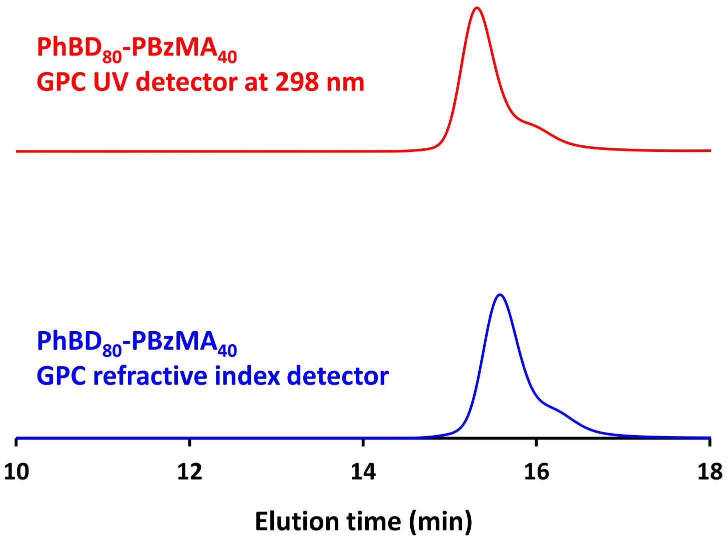


Figure S3. GPC curves obtained for PhBD$_{80}$-PBzMA$_{40}$ diblock copolymers prepared at 40% w/w in *n*-dodecane recorded using either a UV detector tuned to 298 nm (upper red curve) or a refractive index (RI) detector (lower blue curve) [N.B. The UV detector was connected in series with the RI detector, hence these two curves are offset by approximately 30 seconds]. The presence of a low molecular weight sholder in both curves indicates that this feature corresponds to unreacted trithiocarbonate-capped PhBD macro-CTA, rather than non-esterified PhBD precursor (because the latter species does not absorb at 298 nm).

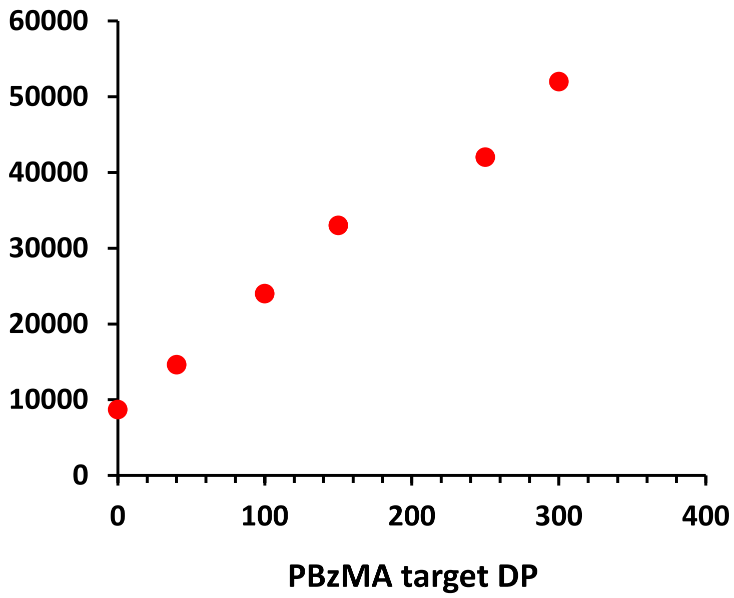


Figure S4. Plot of GPC M_n vs. target PBzMA DP (obtained using THF eluent and a series of PMMA standards) for a series of five $PhBD_{80}$-$PBzMA_x$ diblock copolymers and the corresponding $PhBD_{80}$ macro-CTA prepared at 45% w/w solids in *n*-dodecane.

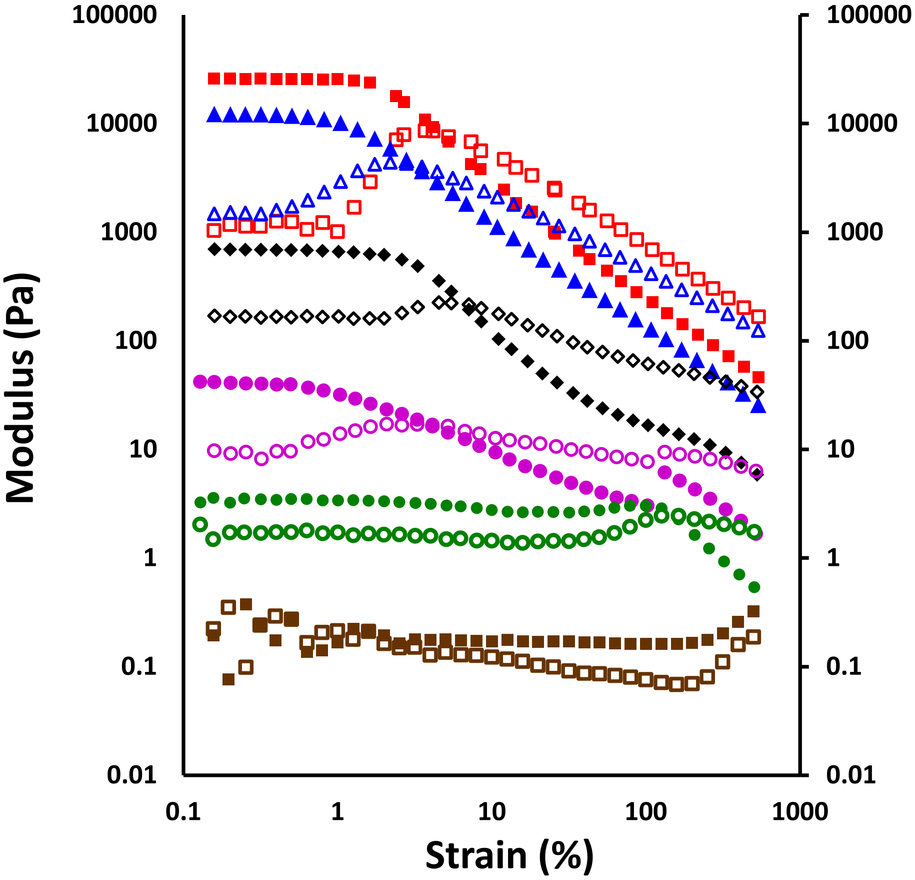


Figure S5. Storage moduli (G'; filled symbols) and loss moduli (G''; open symbols) obtained during a strain sweep conducted on PhBD$_{80}$-PBzMA$_{40}$ worms over a range of copolymer concentrations in *n*-dodecane: 40% w/w (red squares), 30% w/w (blue triangles), 20% w/w (black diamonds), 8% w/w (purple circles), 6% w/w (green circles) and 5% w/w (brown squares). In each case, the angular frequency was fixed at 1.0 rad s^{-1}.

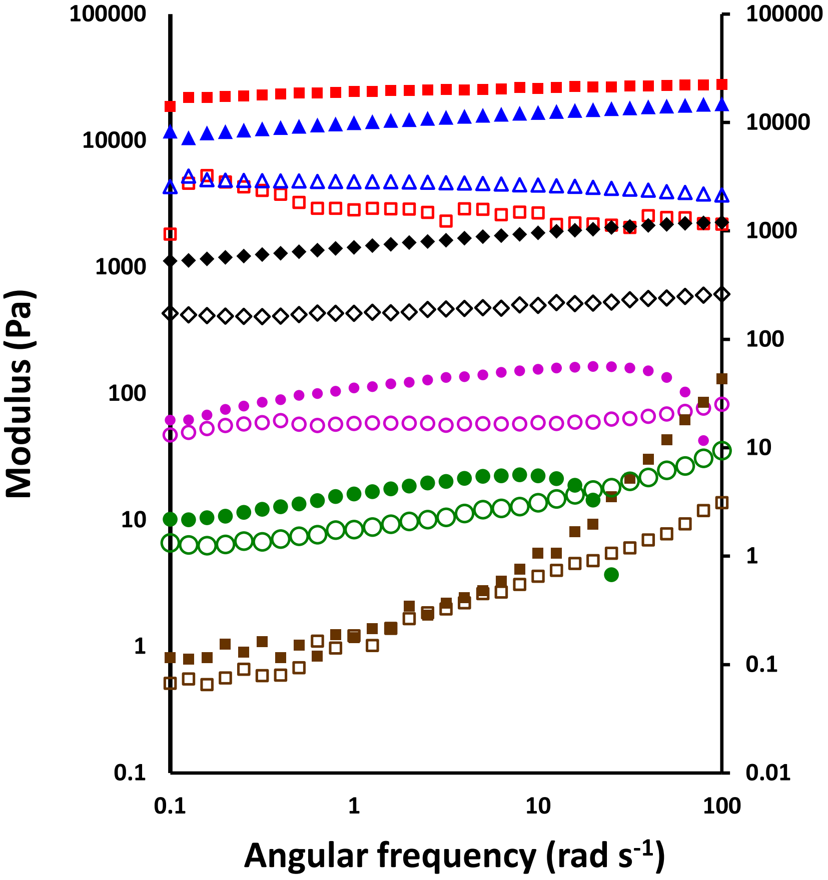


Figure S6. Storage moduli (G'; filled symbols) and loss moduli (G''; open symbols) obtained during a frequency sweep conducted on PhBD$_{80}$-PBzMA$_{40}$ worms over a range of copolymer concentrations in *n*-dodecane: 40% w/w (red squares), 30% w/w (blue triangles), 20% w/w (black diamonds), 8% w/w (purple circles), 6% w/w (green circles) and 5% w/w (brown squares). In each case, the applied strain was 1%.