Supporting Information for:

Comparison of Pseudo-living Character of RAFT Polymerizations Conducted under Homogeneous and Heterogeneous Conditions

Mona Semsarilar, Elizabeth R. Jones and Steven P. Armes*

Experimental Section

Materials. All reagents were purchased from Sigma-Aldrich and used as received unless otherwise noted. 4,4'–Azobis-4-cyanopentanoic acid (ACVA) and 4,4'-azobis-(2-methylpropionitrile) (AIBN) were used as initiators. 4-Cyano-4-(2-phenylethane sulfanylthiocarbonyl)sulfanylpentanoic acid (PETTC) was synthesized as reported previously.[27]

Copolymer Characterization. Molar mass and molar mass distributions of the block copolymers were measured using size exclusion chromatography (SEC); The set-up comprised two 5 μm (30 cm) mixed C columns, a WellChrom K-2301 refractive index detector operating at 950 ± 30 nm, and the eluent was THF [containing 2 v/v % triethylamine and 0.05 w/v % butylhydroxytoluene (BHT)] at a flow rate of 1.0 mL min^{-1}; A series of 10 near-monodisperse linear poly(methyl methacrylates) (M_p ranging from 1,280 to 330,000 g mol^{-1}) were purchased from Polymer Labs and employed as calibration standards with the above refractive index detector. ^{1}H NMR spectra were acquired on a Bruker 250 MHz or 400 MHz in $CDCl_3$. ^{19}F NMR spectra were acquired on a Bruker 250 MHz in CD_3OD. All chemical shifts are reported in ppm (δ). TEM studies were conducted using a Philips CM 100 instrument operating at 100 kV. To prepare TEM samples, 5.0 μL of a dilute aqueous copolymer solution was placed onto a carbon-coated copper grid, stained with uranyl formate and dried under ambient conditions. DLS measurements were conducted using a Malvern Instruments Zetasizer Nano series instrument equipped with a 4 mW He-Ne laser operating at 633 nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system. Aqueous electrophoresis measurements were performed on a 0.01 wt% aqueous copolymer solution using the same Malvern Instruments Zetasizer Nano series instrument. The solution pH was adjusted by the addition of 0.01 M HCl or 0.01 M KOH using an autotitrator. The UV-Visible spectra were recorded with a 1.0 cm quartz cuvette using a Carry 3 Bio spectrometer operating at a scan speed of 600 nm min^{-1}.

Synthesis of poly(methacrylic acid) (PMAA) macro-CTA. In a typical experiment, a round-bottomed flask was charged with MAA (5.00 g; 58.0 mmol), PETTC (300 mg; 0.890 mmol), ACVA (50.0 mg, 0.179 mmol) and ethanol (5.00 g). The sealed reaction vessel was purged with nitrogen and placed in a pre-heated oil bath at 70˚C for 3 h. The resulting PMAA macro-CTA (MAA conversion = 100 %; after methylation, M_n = 9,000 g mol^{-1}, M_w = 11,000 g mol^{-1}, M_w/M_n = 1.19) was purified using dialysis, first against a 1:1 water: methanol mixture and then against pure deionized water. The polymer was isolated by freeze-drying from this aqueous solution overnight. A mean DP of 70 was calculated for this macro-CTA using ^{1}H NMR by comparing the integrated signal intensity due to the aromatic protons at 7.2-7.4 ppm with that due to the methacrylic polymer backbone at 0.4-2.5 ppm.

Synthesis of poly(2-(dimethylamino)ethyl methacrylate) (PDMA) macro-CTA. A round-bottomed flask was charged with 2-(dimethylamino)ethyl methacrylate (DMA; 10.0 g, 32 mmol), PETTC (0.216 g, 0.64 mmol), ACVA (36 mg, 0.127 mmol), and THF (10.0 g) (target DP = 50). The sealed reaction vessel was purged with nitrogen and placed in a preheated oil bath at 70 °C for 6 h. The resulting polymer (monomer conversion = 80%; M_n = 6000 g mol^{-1}, M_w/M_n = 1.22) was purified by precipitation into excess petroleum ether. The mean degree of polymerization (DP) of this PDMA macro-CTA was calculated to be 43 using ^{1}H NMR spectroscopy by comparing the integrated signals corresponding to the aromatic protons at 7.2−7.4 ppm with those due to the methacrylic polymer backbone at 0.4−2.5 ppm.

Synthesis of poly(methacrylic acid)-poly(2,2,2-trifluoroethyl methacrylate) (PMAA-PTFEMA) diblock copolymer particles via RAFT dispersion polymerization in ethanol at 70^{o}C. In a typical 20 w/w % alcoholic dispersion polymerization of $PMAA_{70}$-$PTFEMA_{300}$, TFEMA (1.50 g; 8.90 mmol), AIBN (2.00 mg; 0.012 mmol) and $PMAA_{70}$ macro-CTA (0.179 g; 0.030 mmol) were dissolved in ethanol (6.72 g). The reaction mixture was sealed in a round-bottomed flask, purged with nitrogen for 15 min. and then placed in a pre-heated oil bath at 70˚C for 24 h.

Synthesis of poly(2-(dimethylamino)ethyl methacrylate)-poly(2,2,2-trifluoroethyl methacrylate) (PDMA-PTFEMA) diblock copolymer particles via RAFT dispersion polymerization in ethanol at 70°C. In a typical 20 w/w % alcoholic dispersion polymerization of $PDMA_{43}$-$PTFEMA_{300}$, TFEMA (1.50 g; 8.90 mmol), AIBN (2.00 mg; 0.012 mmol) and $PDMA_{43}$ macro-CTA (0.200 g; 0.030 mmol) were dissolved in ethanol (6.81 g). The reaction mixture was sealed in a round-bottomed flask, purged with nitrogen for 15 min. and then placed in a pre-heated oil bath at 70˚C for 24 h. Kinetic studies were conducted as follows. TFEMA (2.00 g; 11.9 mmol), AIBN (2.60 mg; 0.015 mmol) and $PDMA_{94}$ macro-CTA (0.586 g; 0.039 mmol) were co-dissolved in ethanol (10.35 g). This reaction mixture was sealed in a round-bottomed flask, purged with nitrogen for 30 minutes, and then placed in a pre-heated oil bath at 70 ˚C. Aliquots (0.40 mL) were extracted on an hourly basis under a positive nitrogen atmosphere for 24 h. UV-visible spectra were recorded by diluting 20 μL of an aliquot in 2.0 mL ethanol. Each reading was repeated three times and the average value was reported.

Synthesis of poly(2-(dimethylamino)ethyl methacrylate)-poly(2,2,2-trifluoroethyl methacrylate) (PDMA-PTFEMA) diblock copolymer particles via RAFT dispersion polymerization in ethanol at 70°C. In a typical 20 w/w % alcoholic dispersion polymerization of $PDMA_{94}$-$PTFEMA_{300}$, TFEMA (1.50 g; 8.90 mmol), AIBN (2.00 mg; 0.012 mmol) and $PDMA_{94}$ macro-CTA (0.440 g; 0.030 mmol) were dissolved in ethanol (7.77 g). The reaction mixture was sealed in a round-bottomed flask, purged with nitrogen for 15 min. and then placed in a pre-heated oil bath at 70˚C for 24 h.

Synthesis of poly(methacrylic acid)-poly(2,2,2-trifluoroethyl methacrylate) (PMAA-PTFEMA) diblock copolymer particles via RAFT solution polymerization in THF at 70°C. In a typical 20 w/w % alcoholic solution polymerization of $PMAA_{70}$-$PTFEMA_{300}$, TFEMA (1.00 g; 5.90 mmol), AIBN (1.30 mg; 0.008 mmol) and $PMAA_{70}$ macro-CTA (0.119 g; 0.020

mmol) were dissolved in THF (4.48 g). The reaction mixture was sealed in a round-bottomed flask, purged with nitrogen for 15 min. and then placed in a pre-heated oil bath at 70˚C for 14 h. At this point, a further charge of AIBN (1.30 mg; 0.008 mmol) dissolved in ethanol (0.10 mL) was added as a fresh radical source. Reactions were quenched after 24 h, at which point high monomer conversions were observed.

Synthesis of poly(2-(dimethylamino)ethyl methacrylate)-poly(2,2,2-trifluoroethyl methacrylate) (PDMA-PTFEMA) diblock copolymer particles via RAFT solution polymerization in THF at 70°C. In a typical 20 w/w % alcoholic solution polymerization of $PDMA_{94}$-$PTFEMA_{300}$, TFEMA (1.00 g; 4.95 mmol), AIBN (1.30 mg; 0.008 mmol) and $PDMA_{94}$ macro-CTA (0.293 g; 0.020 mmol) were dissolved in ethanol (5.18 g). The reaction mixture was sealed in a round-bottomed flask, purged with nitrogen for 15 min. and then placed in a pre-heated oil bath at 70˚C for 24 h.

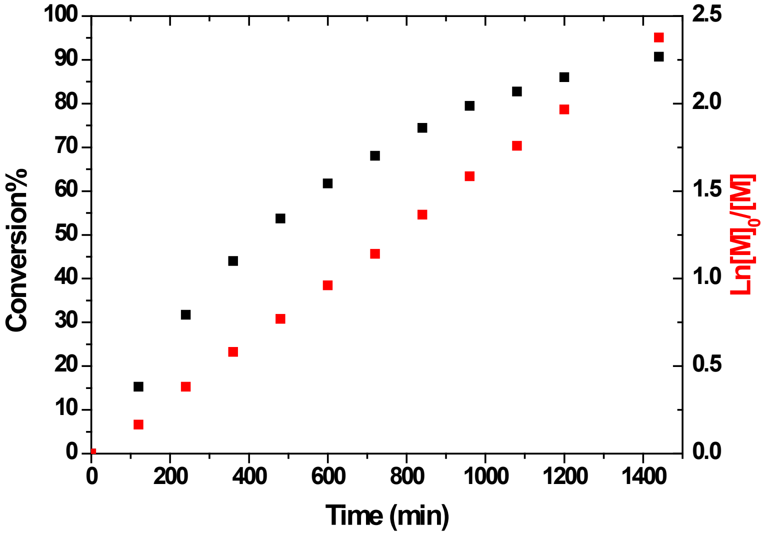


Figure S1. ^{1}H NMR kinetic data obtained for the RAFT dispersion polymerization of TFEMA at 20 % w/w solids in ethanol using a $PMAA_{70}$ macro-CTA at 70°C. The targeted diblock composition was $PMAA_{70}$-$PTFEMA_{300}$ and the macro-CTA/AIBN molar ratio was 2.50.

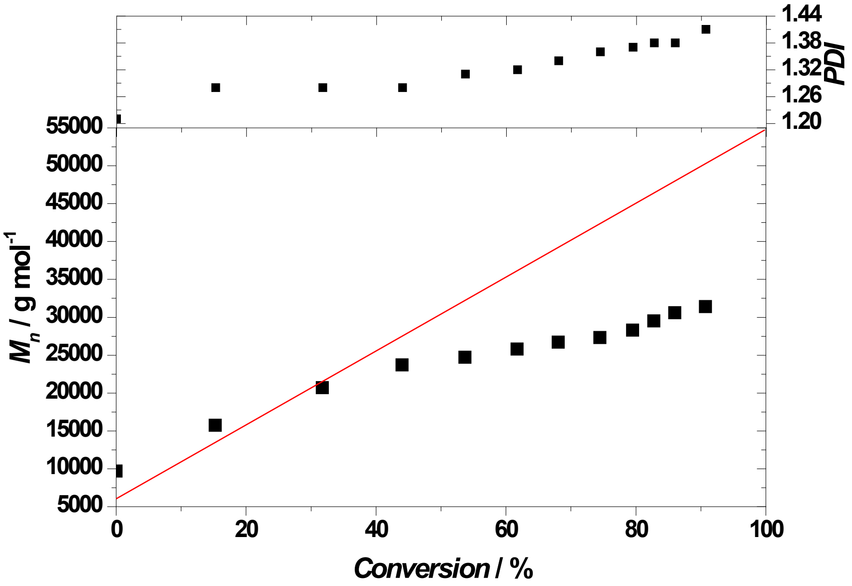


Figure S2. Evolution of number-average molecular weight M_n (vs. poly(methyl methacrylate) calibration standards) and polydispersity (M_w/M_n) with monomer conversion for the RAFT dispersion polymerization of TFEMA at 20 % w/w solids in ethanol at 70°C, as judged by THF GPC. The targeted diblock composition was PMAA$_{70}$-PTFEMA$_{300}$ and the macro-CTA/AIBN molar ratio was 2.50. The apparently poor pseudo-living character observed for this RAFT polymerization is mainly due to a GPC artifact, see main text.

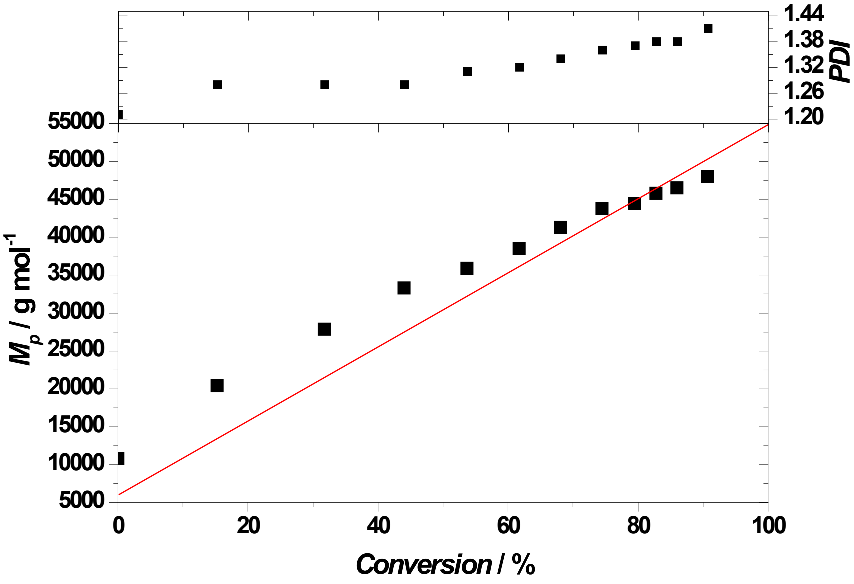


Figure S3. Evolution of peak molecular weight M_p (vs. poly(methyl methacrylate) calibration standards) and polydispersity (M_w/M_n) with monomer conversion for the RAFT dispersion polymerization of TFEMA at 70°C in ethanol at 20% solids, as determined by THF GPC analysis. The targeted diblock composition was PMAA$_{70}$-PTFEMA$_{300}$.

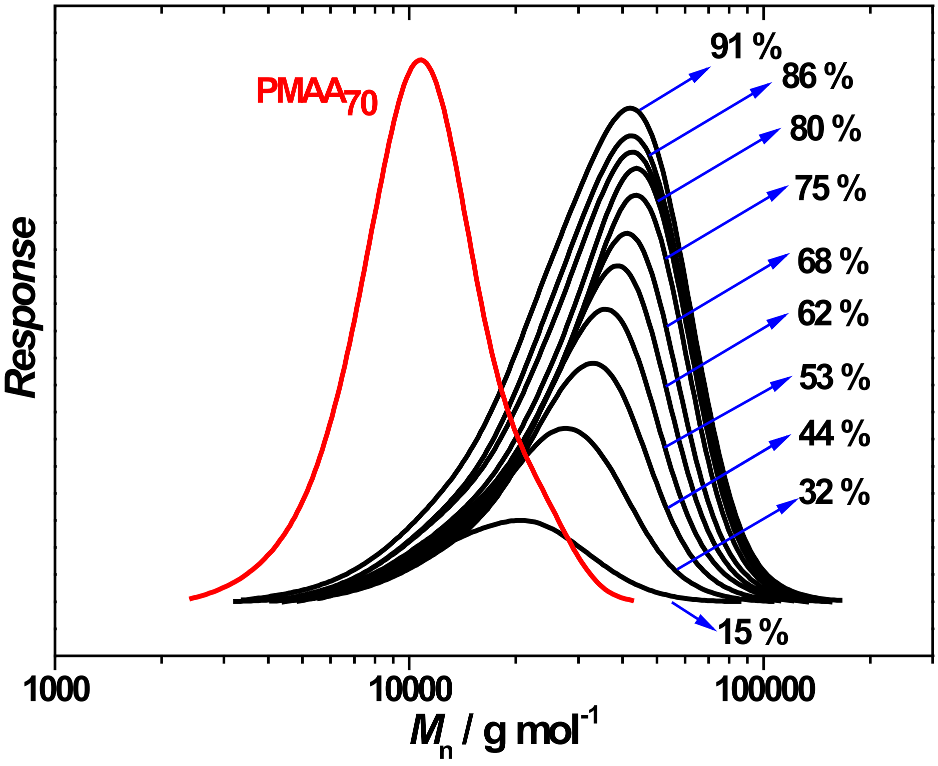


Figure S4. GPC traces (refractive index detector) recorded during the RAFT dispersion polymerization of TFEMA at 20 % w/w solids in ethanol at 70°C using a PMAA$_{70}$ macro-CTA and a macro-CTA/AIBN molar ratio of 2.50. The targeted diblock composition was PMAA$_{70}$-PTFEMA$_{300}$. In this case the macro-CTA has a more comparable molecular weight to the final diblock copolymer than the PDMA$_{43}$ macro-CTA shown in Figure 4 (see main text). Thus only pronounced tailing to low molecular weight is observed, rather than bimodality.

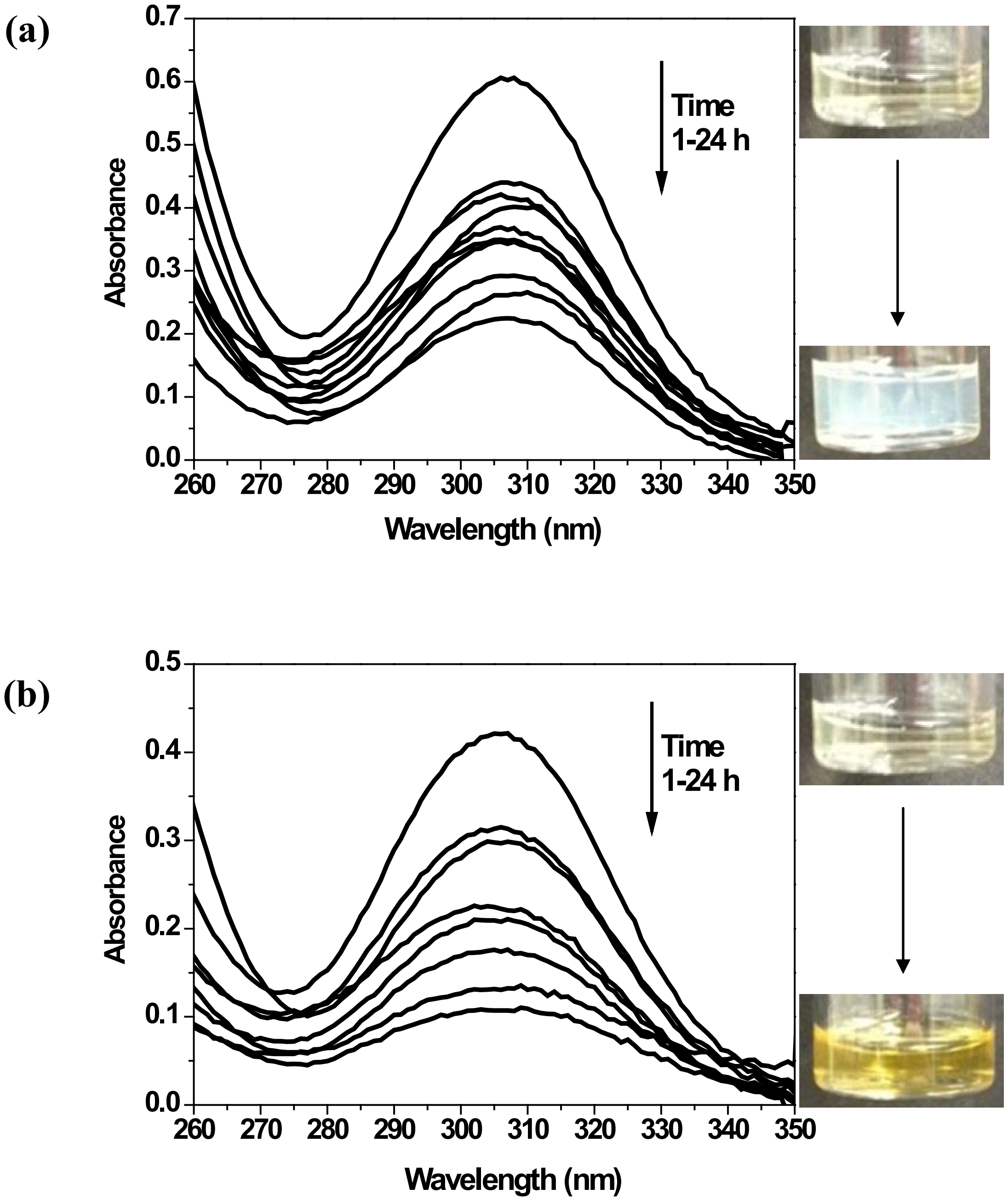


Figure S5. (a) UV-visible absorption spectra recorded during the RAFT dispersion polymerization of TFEMA at 20 % w/w solids in ethanol at 70°C when targeting a final diblock composition of PDMA$_{94}$-PTFEMA$_{300}$. The inset photo shows the relatively low turbidity observed for the last kinetic sample obtained at 91% conversion. (b) UV-visible absorption spectra recorded during the RAFT solution polymerization of TFEMA at 20 % w/w solids in THF at 70°C using a PDMA$_{94}$ macro-CTA when targeting a final diblock composition of PDMA$_{94}$-PTFEMA$_{300}$. The inset photo shows the transparent orange reaction solution observed for the last kinetic sample obtained at 91% conversion.

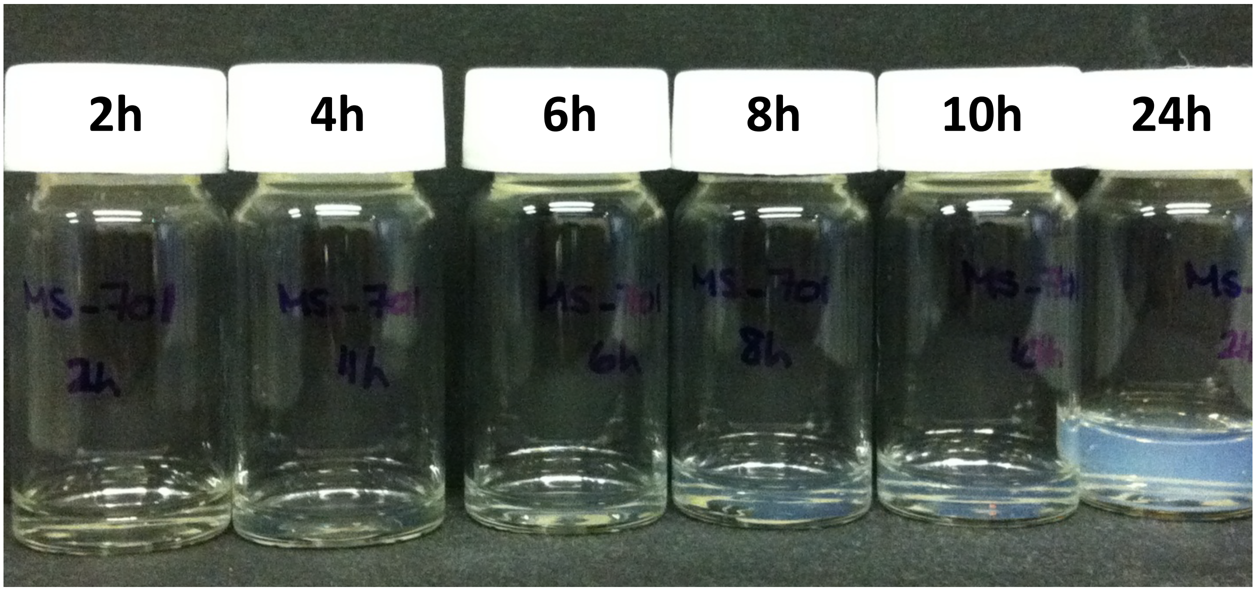


Figure S6. Digital photographs obtained for the RAFT dispersion polymerization of TFEMA when targeting a diblock composition of $PMAA_{70}$-$PTFEMA_{300}$.

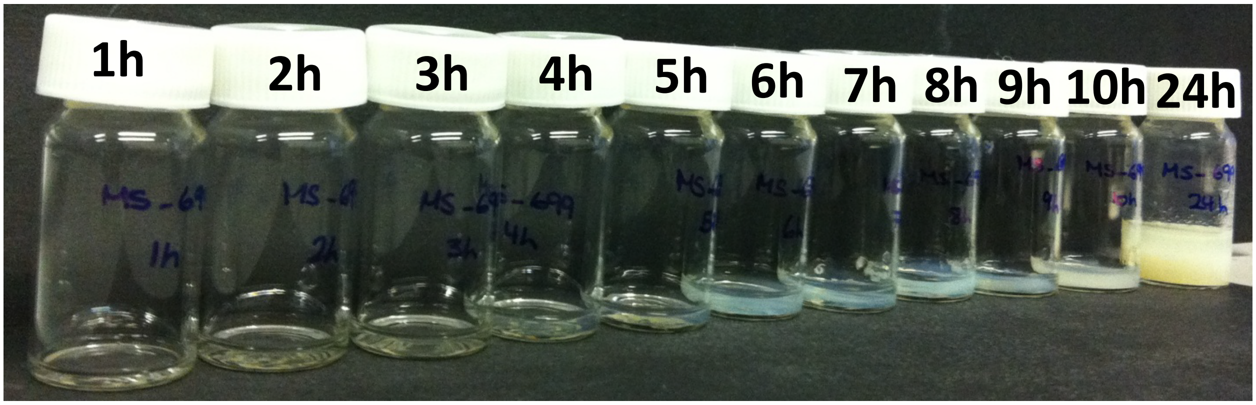


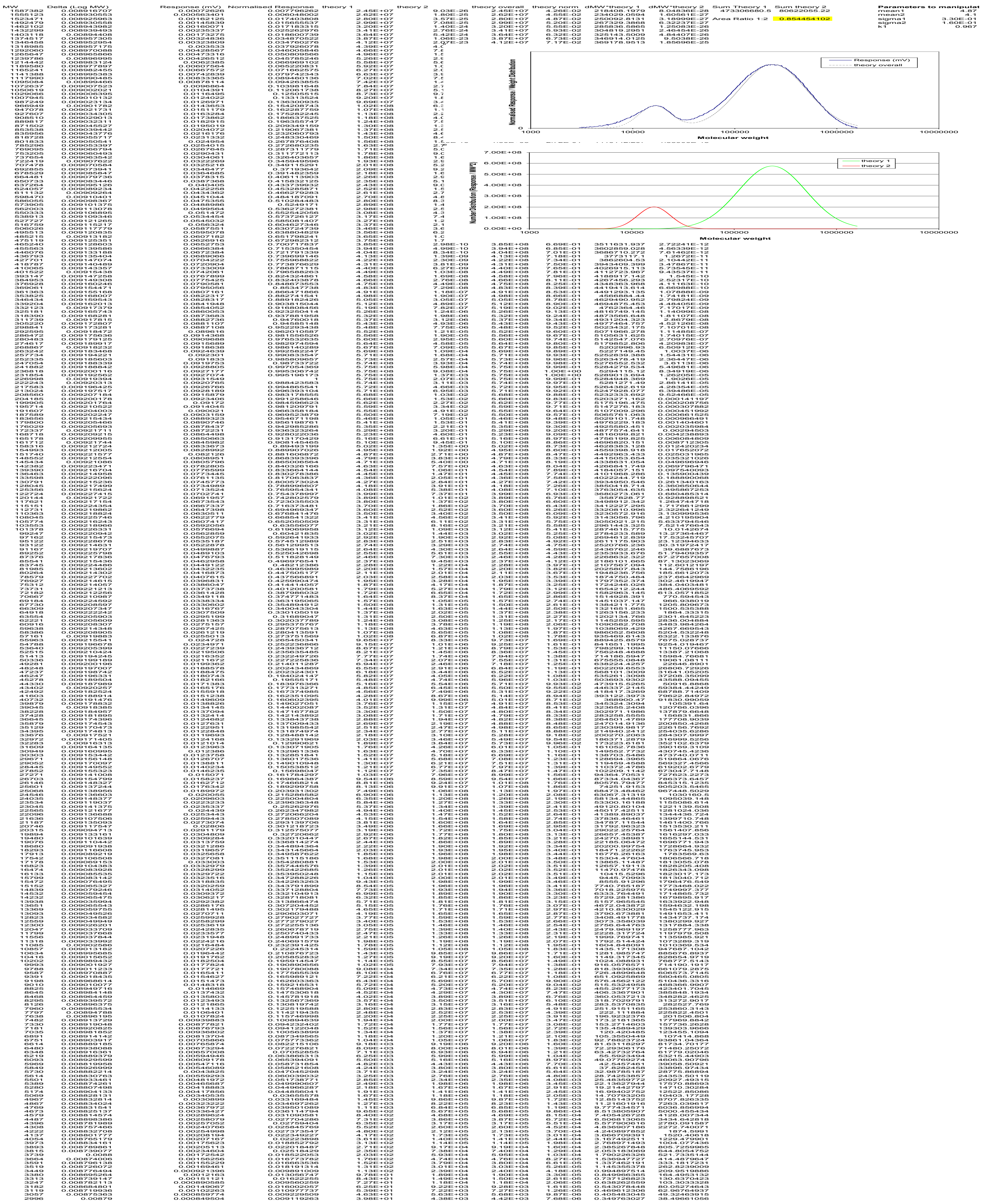
Figure S7. Digital photographs obtained for the RAFT dispersion polymerization of TFEMA when targeting a diblock composition of $PDMA_{43}$-$PTFEMA_{300}$.

Table S1. Summary of RAFT dispersion and solution polymerization of PTFEMA conducted in ethanol or THF, respectively.

Solvent Type	**Macro-CTA**	**Targeted DP_{PTFEMA}**	**Conv. %**	**Actual DP of PTFEMA**	**M_n (g mol^{-1})**	**M_n/M_w**
ethanol	$PDMA_{94}$	300	94	282	24,000	1.57
THF	$PDMA_{94}$	300	98	294	24,500	1.56
ethanol	$PMAA_{70}$	300	91	273	24,000[a]	1.63
THF	$PMAA_{70}$	300	91	273	26,000[a]	1.56

[a] GPC results obtained after methylation of the PMAA block (vs. PMMA standards).

S???. Excel spreadsheet used for GPC peak deconvolution.



MW	Delta (Log MW)	Response (mV)	Normalised Response	theory 1	theory 2	theory overall	theory norm	dMW*theory 1	dMW*theory 2
1587382	0.008916707	0.00072626	0.007796262	2.45E+07	9.03E-26	2.45E+07	4.26E-02	218408.1979	8.04836E-28
1555123	0.008930553	0.000563401	0.006048002	2.62E+07	1.80E-25	2.62E+07	4.55E-02	234029.0594	1.60561E-27
1523471	0.008925963	0.00162125	0.017403808	2.80E+07	3.57E-25	2.80E+07	4.87E-02	250092.8131	3.18999E-27
1492479	0.008930558	0.00145839	0.015655537	2.99E+07	7.08E-25	2.99E+07	5.20E-02	267329.3868	6.32237E-27
1462102	0.008943982	0.00160071	0.017183315	3.20E+07	1.40E-24	3.20E+07	5.55E-02	285836.5865	1.25083E-26
1432299	0.008939493	0.00235337	0.025262976	3.41E+07	2.76E-24	3.41E+07	5.93E-02	304819.2951	2.46454E-26
1403118	0.00894408	0.00173275	0.018600739	3.64E+07	5.42E-24	3.64E+07	6.32E-02	325143.5009	4.84407E-26
1374517	0.008957305	0.00324836	0.034870522	3.87E+07	1.06E-23	3.87E+07	6.73E-02	346914.0125	9.5038E-26
1346458	0.008952954	0.00323809	0.034760276	4.12E+07	2.07E-23	4.12E+07	7.17E-02	369178.9513	1.85696E-25

Sum Theory 1	Sum theory 2
473306680.5	80622055.22
Area Ratio 1:2	0.854454102

Parameters to manipulat	
mean1	4.87
mean2	4.1
sigma1	3.30E-01
sigma2	1.60E-01
k1	0.967